WHITE PAPER

THE EVOLUTION OF METALLOCENE LLDPE RESINS

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Find out how the latest generation of mLLDPE resins improve film processing and performance
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THE LATEST EVOLUTION IN METALLOCENE CATALYST TECHNOLOGY HAS DELIVERED LINEAR LOW DENSITY POLYETHYLENE (MLLDPE) RESINS THAT OFFER SIGNIFICANT IMPROVEMENTS IN PROCESSABILITY, TOUGHNESS AND STIFFNESS THAT AID DOWNGAUGING.

Metallocene linear low density polyethylene (mLLDPE) is increasingly popular with PE resin converters as it enables the production of stronger films with improved properties and that use less material.

mLLDPE is especially suited to flexible packaging – one of the fastest growing sectors of the global PE market.

Consumers have readily transitioned from a range of rigid packaging alternatives to lighter-weight flexible packaging products, driving an increased demand for mLLDPE resins.

This paper describes the different generations of mLLDPE resins and the different technical and performance characteristics of each.

EVOLUTION OF MLLDPE RESINS

Since the introduction in the 1990s, metallocene LLDPE resins have continued to evolve and improve. mLLDPE is produced in a low-pressure polymerisation process using a metallocene catalyst to copolymerise ethylene and a comonomer such as 1-hexene. Metallocene catalysts are effective because they provide greater control over the polymerisation reaction. The discovery of these catalysts led to a break-through in the control of the crystalline structure or “architecture” of polyethylene.

In particular, resins made using metallocene catalysts have become known for exceptional impact strength and sealability compared to conventional LLDPE resins. These properties were achieved by improved control over the locations of the short chain branches in the polyethylene chain. Figure 1 shows that conventional LLDPE resins have short chain branches predominantly located in the lower molecular weight chains whereas first generation mLLDPE resins have branches distributed evenly across the whole molecular weight distribution. This is of particular importance to the mechanical properties as only long chains containing short chain branches are able to act as tie molecules, which hold together the tertiary semi-crystalline structure of the polymer, providing toughness and creep resistance.

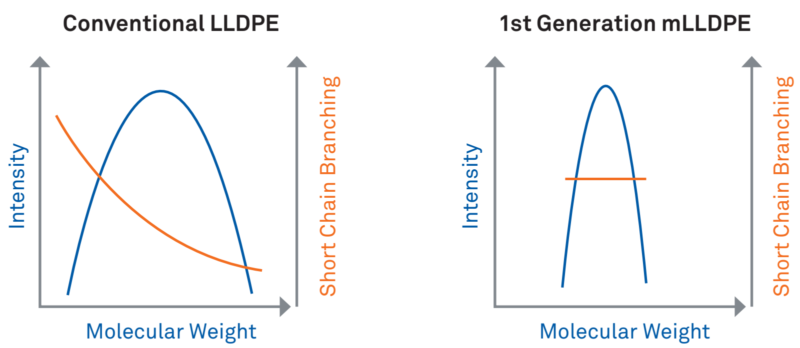

Figure 1. **Molecular weight and short chain branching distribution for conventional (Ziegler-Natta) LLDPE and first generation mLLDPE.**

THIRD GENERATION mLLDPE RESINS PROVIDE IMPROVEMENTS IN PROCESSABILITY AND DOWNGAUGING

The first generation of metallocene catalysts also produce highly uniform polyethylene molecules with very consistent molecular weight. Figure 1 illustrates that the molecular weight distribution (MWD) of these mLLDPE resins is significantly narrower compared to conventional LLDPE. The narrow molecular weight distribution typically caused these first generation metallocene resins to be harder to process than regular LLDPE or LDPE. With fewer shorter molecules, these resins required higher extruder motor loads, generated higher head pressures, increased shear heating and had a higher propensity to experience melt fracture.

In addition, as these resins have fewer longer molecules, they tended to exhibit lower melt strength and reduced bubble stability. The more challenging processability and lower output rates have impeded the uptake of these products in some applications.

The second generation of metallocene resins was designed to more effectively compete with LDPE by addressing the processability issues. To improve processability, these resins have a broader molecular weight distribution and contain low levels of long chain branches. While these modifications improve processability, they also reduce the toughness and sealing performance.

The recently introduced third generation metallocene catalyst (used by Qenos to produce the Alkamax mLLDPE range) addresses the technical challenges faced by earlier generations and provides excellent performance characteristics and easier processability. This improvement is achieved through tailoring the short chain branching distribution by inserting branching preferentially in the high molecular weight chains (Figure 2). This dramatically increases the number of tie chain molecules available for holding the structure together, providing toughness. At the same time, the MWD for the third generation mLLDPE is broader than for first generation mLLDPE and more like conventional LLDPE. The result is a resin family with optimised processability and exceptional toughness (Figure 3).

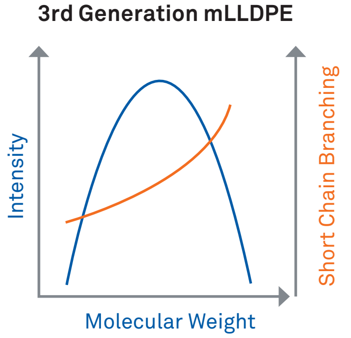

Figure 2. Molecular weight and short chain branching distribution for third generation mLLDPE.

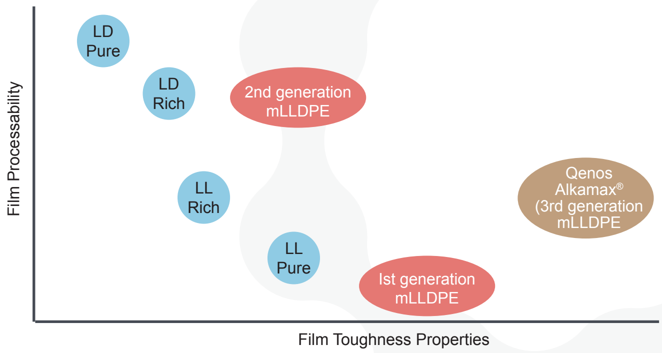

Figure 3. Evolution of PE resins for film processability and film toughness

PERFORMANCE COMPARISON OF DIFFERENT mLLDPE RESINS

The performance of a resin depends principally on its molecular architecture. Resin manufacturers seek to optimise their product, producing resins with specific properties to meet target performance requirements. The development of the third generation catalyst technology unlocks additional flexibility in the molecular design of the resin.

Processability

The ease of processing a metallocene resin is primarily a function of its rheological properties, which are controlled by the molecular structure. Through their typically narrow MWD, first generation mLLDPE resins have been found to be more challenging to process, leading to high head pressure and even melt fracture at high output. Incorporation of a high performance process aid may be used to mitigate melt fracture.

The broader MWD of a third generation mLLDPE enables significantly improved processability. Figure 4 shows a comparison of Alkamax grade ML1810PN and a first generation C6 mLLDPE resin in a representative film structure with both resins blended with 20% LDPE. The superior processability of ML1810PN results in lower motor load (extruder power) requirements and head pressures, delivering a lower cost of production. Additionally the lower propensity to experience melt fracture reduces the need for a process aid masterbatch.

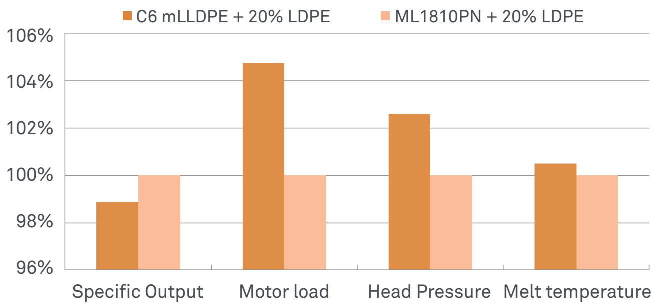

Figure 4. Processability of Alkamax (ML1810PN) mLLDPE resin and a first generation C6 mLLDPE resin.

Dart impact strength

Toughness is a critical film property in many applications. Dart impact strength testing (Figure 5) shows the toughness advantage of Alkamax ML1810PN over a first generation C6 mLLDPE, particularly in blends with LDPE which are the most common applications for metallocene resins. This improvement results from the optimal incorporation of short chain branches within the polymer chain, leading to a higher concentration of tie molecules.

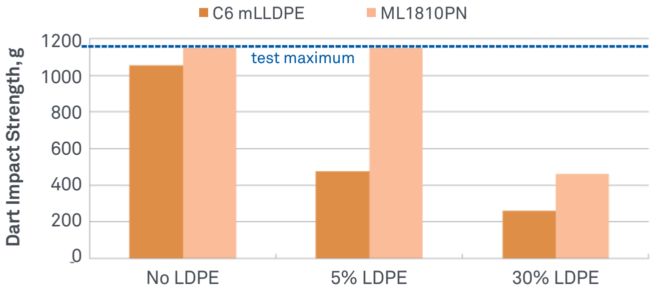

Figure 5. Dart impact strength of Alkamax (ML1810PN) mLLDPE resin and a first generation C6 mLLDPE resin in blends with LDPE.

Stiffness/toughness balance

The balance of stiffness and toughness is important in many packaging applications. Dart impact strength is the typical indicator of toughness. Secant modulus, measured by a tensile test, is the typical indicator of film stiffness (Figure 6). Higher stiffness typically improves web handling in film processing operations such as printing, laminating and bag making. Stiffer film also assists with the filling stage as it better maintains the required bag shape.

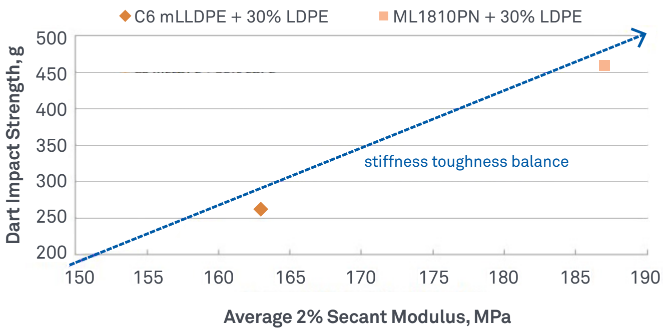

Figure 6. Toughness and stiffness of Alkamax (ML1810PN) resin and a first generation mLLDPE resin.

Creep Resistance

Another property related to stiffness is creep resistance. Many materials including polyethylene can stretch over time when put under stress in a process known as creep. Metallocene resins, particularly the third generation resins, have improved creep resistance properties. This makes these resins particularly suitable for Heavy Duty Sack applications, where the packaging must contain heavy loads for long periods during loading, transport and storage without spillage.

Downgauging and production cost reduction

The combination of higher toughness and stiffness enables further downgauging – allowing products to be produced using less resin. Film extruded at a thinner gauge can maintain the required strength and stiffness required by the converting and packaging operations. In some cases, film thickness can be reduced by up to 20% compared to a standard LLDPE resin.

Additionally the superior strength of third generation mLLDPE resins can allow the incorporation of lower strength recycled materials.

Sealing characteristics

Repeatable sealing over a wide range of conditions is critical in efficient manufacturing, especially in form, fill and seal packaging lines. mLLDPE polymers offer excellent seal and hot tack properties that greatly help ensure seal integrity.

Third generation mLLDPE resins have good hot tack strength at lower temperatures and over a wider range, as shown in Figure 7. The broad sealing window and high seal strength deliver superior package integrity and reduced risk of leaking, while maintaining high throughput in sealing operations.

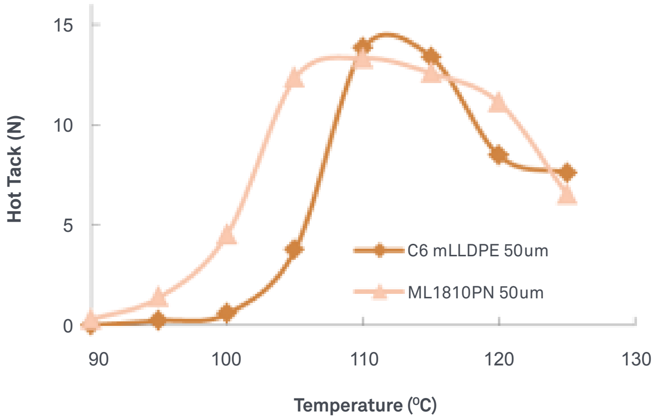

Figure 7. Hot tack performance of ML1810PN and a first generation C6 mLLDPE.

HOW THE RESIN SUPPLIER CAN HELP?

Metallocene catalysts allow the production of resins with specific properties.

It's important to consider the following characteristics when assessing different types of mLLDPE resins:

- How easy is the resin to process on the specific equipment?
- Are the performance characteristics of the resin suited for the product being manufactured?
- Can the resin be blended and co-extruded with other grades to improve film properties across a range of applications?
- Will the resin support further downgauging?
- What technical advice and insights can be offered by the resin supplier?

The Qenos Alkamax mLLDPE range of resins is manufactured using the latest third generation catalyst technology. The resins are specially designed and formulated to provide superior mechanical properties and ease of processability.

Qenos offers a range of metallocene linear low-density polyethylene grades designed for applications from stretch wrap, laminates, frozen food and ice bags to industrial packaging, heavy duty sacks, mulch and silage.

Figure 8. Third generation mLLDPE resins are being used in films requiring exceptional toughness.

Qenos has a team of PE resin development specialists supported by commercial and laboratory scale film lines. This deep knowledge base and world class facilities are available to support the development of custom formulation solutions for customers.

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