Bimodal Polyethylene Products from UNIPOL™ Single Gas Phase Reactor Using Engineered Catalysts

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Summary: Advanced catalyst engineering from Univation Technologies provides the capability to produce polyethylene with bimodal molecular weight distribution and bimodal composition distribution in a single gas phase reactor. This paper will discuss the structure-property-process relationship for these engineered polyethylene products. Examples of High Density Polyethylene (HDPE) polymers with bimodal molecular weight distribution will demonstrate the utility of the engineered catalysts in high molecular weight film production. Examples of Linear Low Density Polyethylene (LLDPE) polymers with broad comonomer composition distribution will demonstrate the utility of the engineered catalysts for high strength film applications. Examples of HDPE polymers with bidmoal molecular distribution and controlled comonomer distribution will demonstrate the capability of Univation's latest engineered catalysts for high performance pipe applications.

Keywords: bimodal; catalysts; HDPE pipe; molecular weight distribution; polyethyelene

Introduction

In the most general sense, engineered catalysts from Univation Technologies utilize combinatorial catalyst chemistry to produce a series of polyethylene (PE) products that provide attributes of interest for either LLDPE or HDPE polymers. These attributes may include, bimodal molecular weight distribution (BMWD), bimodal comonomer composition distribution (BCD) or a combination of both. In addition, the engineered catalyst technology may incorporate bimodal combinations of linear and long-chain branched molecules.

The breakthrough technology developed by Univation scientists centers around the ability to co-support these combinatorial catalysts and avoid the unwanted interactions between the components that renders them ineffective [1]. The co-supported nature of these catalysts also leads to more intimate mixing of the bimodal components at a molecular level and thus to improved homogeneity in product properties relative to prior art with co-fed, independently supported systems [2-7].

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Engineered Catalysts for Bimodal MWD HDPE Film Resin

Over the last few decades, bimodal MWD HDPE resins have gained considerable popularity over their unimodal counterparts due to a better balance of processability and properties. As shown in Figure 1, one way to improve physical properties in standard unimodal MWD resins is to increase molecular weight (lowering MI). However, processability suffers.

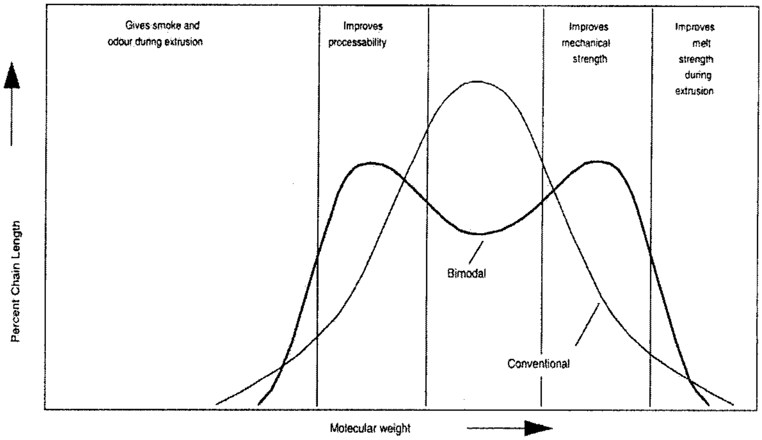

Figure 1. Bimodal MWD HDPE Design Concept, MMW/LMW Split and Spread Control Processability and Property Balance (Graphic Courtesy of Nexant Inc./Chem Systems).

Bimodal resins, on the other hand, have the best of both worlds: low molecular weight (LMW) species for processability and high molecular weight (HMW) species for properties. The performance of the bimodal resins can be further enhanced by preferentially incorporating comonomer in the HMW portion of the molecular weight distribution. This results in higher concentration of tie-chains which are important for end use performance [9-11]. One of the main drawbacks to the widespread use of bimodal HDPE technology has been the need to use two dedicated staged (or tandem) slurry reactors. The advent of metallocene technology has provided the breakthrough needed to produce bimodal resins in a single reactor.

There are many advantages to using single reactor bimodal technology vis-à-vis dual reactor systems. Lower investment costs, single reaction environment (easier simpler to control), less process complexity, intimate mixing of high and low molecular weight components (improved product quality), simplifed start-ups and shut-downs are examples of the advantages.

Figure 2 provides a pictorial view of the SEC-MWD data for two example bimodal MWD HDPE polymers that can be produced with engineered catalyst technology relative to a commercial tandem slurry bimodal HDPE.

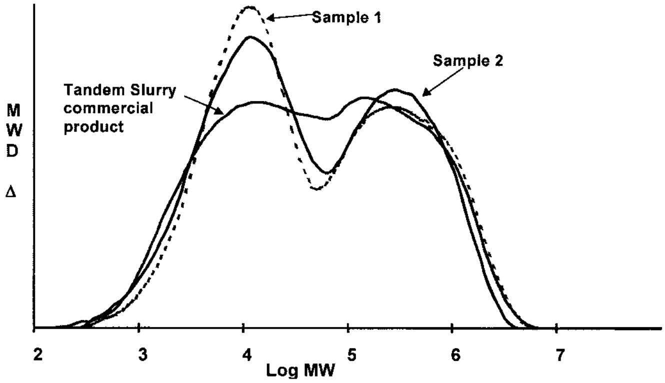

Figure 2. GPC of Two AEC Bimodal HDPE Polymers vs. Tandem Slurry Product.

Table 1 below provides data comparing the bimodal HDPE film generated with a Univation catalyst relative to a conventional unimodal chromium catalyzed polymer and a tandem slurry Z/N catalyzed polymer. It is clear from this comparison that the engineered catalyst product is fully equivalent to the best of class bimodal tandem slurry Z/N product and offers significantly improved dart impact versus the unimodal MWD product.

Table 1. Film Property Comparison for Different HDPE Technologies.
(50 mm Alpine extruder, 100 mm die diam, 1.0 mm die gap, 390-415 deg F barrel to die temp set, 120 lb/hr, 4:1 BUR, 28 inch stalk height).

HMW-HDPE Product	Unimodal (Cr-based) HMW-HDPE	Commercial Slurry Staged Reactor	Univation Bimodal Single Reactor
Resin Properties			
Flow Index, dg/min	9.5	8.5	6.2
Density, g/cc	0.950	0.950	0.950
Film Processibility			
Melt Pressure, psi	6650	6180	6250
Melt Temperature, F	411	419	408
Motor Load, %	48	46	46
Bubble Stability by Max. Draw speed, ft/min	> 300	260	> 300
Film Properties @ 1.0 mil			
Dart Impact, g	237	400	429
Elmendorf Tear, MD g/mil	17	29	27
Elmendorf Tear, TD g/mil	201	134	184
Film Properties @ 0.5 mil			
Dart Impact, g	204	438	444
Elmendorf Tear, MD g/mil	11	23	20
Elmendorf Tear, TD g/mil	52	76	57

Engineered Catalyst for BOCD LLDPE Film Products

The Univation engineered catalysts build on concepts learned from commercial metallocene polymer developments with Univation HPR and EZP mLLDPE. Univation HPR mLLDPE is designed to have narrow CD and MWD to maximize film toughness characteristics. Univation EZP mLLDPE has been designed to provide processability approaching that of a high pressure LDPE while maintaining the toughness attributes of a conventional Z/N LLDPE. Knowledge gained with blends of these single component metallocene catalyzed polymers has enabled Univation to design products with a superior property balance. The ability to produce "tailor-made" polymers with combinations of single site catalysts was recognized early in the development of metallocene catalysts. In USP 5,382,630 granted to Stehling, Speed, and Welborn of Exxon Chemical (now ExxonMobil Chemical), the concept of blending mPE components with different comonomer compositions to produce bimodal composition distribution (BCD) and/or bimodal molecular weight distribution (MWD) polymers with enhanced physical properties was recognized. With metallocene catalyzed ethylene polymers, the inventors showed that it is possible to produce blends where comonomer composition distribution increases with increasing molecular weight. The placement of the comonomer in these polymers as a function of molecular weight is orthogonal, or at right angles to, prior-art Z/N catalyzed LLDPE as depicted by lines D, E and F in Figure 3.

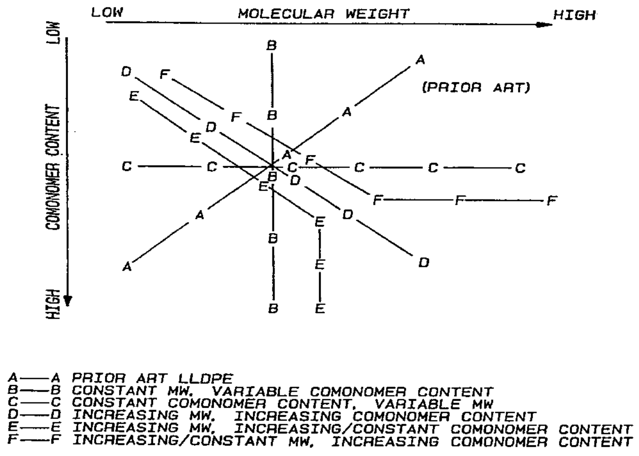

Figure 3. Various composition Distributions as described in US Patent 5,382,630 by Stehling, Speed and Welborn.

These LLDPE products are referred to as broad orthogonal composition distribution (BOCD) polymers. LLDPE blends generated with components that result in broad orthogonal composition distribution were shown to have synergistically improved tear strength relative to the individual components making up the blend. This behavior has been reported by others in the field as well [8-9].

Building on the blend concepts patented by Stehling et al, Univation has been able to tailor a combinatorial catalyst system to produce LLDPE film with superior Elmendorf tear and dart impact characteristics. As noted earlier, the breakthrough capability of co-supporting these combinatorial catalysts has enabled this development to move beyond physical polymer blends to reactor-only products. Polymers with bimodal composition distribution and narrow MWD (BCD polymers) and polymers with bimodal MWD in combination with reversed comonomer distribution (BOCD) have been produced. Figure 4 provides data on the cross fractionation of molecular weight as a function of composition distribution for an example BOCD product. The data was collected by first fractionating the polymer by composition distribution and subsequently measuring the molecular weight of the individual fractions.

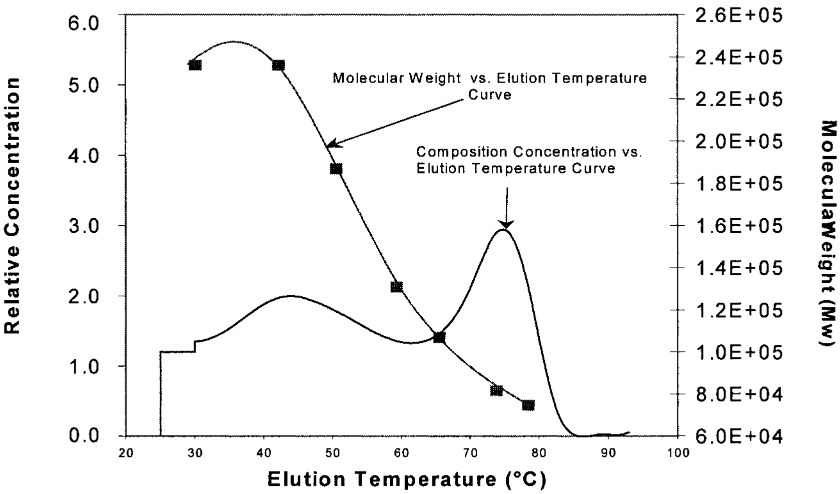

Figure 4. Example of DOCD LLDPE via Engineered Catalyst.

Table 2. Univation Engineereed Catalyst LLDPE Product Properties vs. Commerical Controls (All products utilize hexene as comonomer. All films produced at nominal 0.75 mil gauge with 2.5 BUR, 60 mil die gap, 6" die diameter, 400 F, at 10 lb/hr/in rate).

Film Property	**UTEC BOCD Product**	**Conventional metallocene LLDPE**	**Conventional Z/N LLDPE**
Melt Index, I_2 (dg/min)	0.80	1.03	1.03
Melt Flow Ratio, I_{21}/I_2	29.6	17.6	28.4
Density (g/cc)	0.918	0.919	0.9185
Tensile Strength (psi)			
MD	10060	10010	8650
TD	7180	8570	6590
Dart Impact , g/mil	730	810	160
Puncture Force, lb/mil	13.0	15.2	11.1
Elmendorf Tear (g/mil)			
MD	440	250	370
TD	630	540	830
Secant Modulus (kpsi)			
MD	26.0	23.3	26.4
TD	30.9	26.9	30.3

The appropriate selection of a catalyst pair is critical to the performance and commercial acceptability of a BOCD LLDPE system operating in a single reactor environment. In particular, the appropriate pair should exhibit the following characteristics: a) One component must incorporate comonomer exceptionally well while the other incorporates little or no comonomer at the same gas composition in the reactor. b) Both components must have good activity under the reactor conditions of interest. c) Both components must have similar molecular weight response characteristics with the higher comonomer incorporator preferentially producing the highest molecular weight. d) The component ligands must be easily synthesized to allow for commercial production economics. e) Long chain branching in the component polymers should be minimized to maximize film impact and tear properties.

The property enhancement made possible through the broad orthogonal composition distribution evidenced in a polymer produced with engineered catalyst technology can be see in Table 2. This data shows how the BOCD polymer is able to move beyond the balance of processing and tear strength of a conventional Z/N polymer while maintaining the high dart impact capability of a narrowly distributed commercial metallocene LLDPE product.

Engineered Catalyst for BOCD Bimodal MWD HDPE Pipe Product

In another example of the utility of the engineered catalyst capability, a product with bimodal MWD and orthogonal comonomer composition distribution has been developed for use in HDPE pressure pipe. As with the film application, bimodal MWD provides a good balance in processing and properties. In addition, it has been recognized by others in the field that HDPE polymers with a "reverse comonomer distribution" (BOCD) design are useful in improving the characteristics that govern long term creep-related properties like SCGR (Slow Crack Growth Resistance) and hydrostatic burst strength [9-11].

The uniform and controllable comonomer incorporation capability of the individual components of the engineered product also allow for the production of bimodal MWD HDPE with this reverse comonomer distribution as indicated in Figure 5. This figure was generated by cross-fractionating the HDPE polymers by MW and then measuring branching frequency on the different MW slices obtained via NMR. The humped profile for comonomer distribution is consistent with that of a typical commercial two stage reactor product.

Properties of an engineered catalyst polymer manufactured with this type of product design is consistent with the needs of a HDPE pressure pipe product. The hydrostatic test results of a Univation bimodal pipe sample (32 mm / SDR 11 pipe, ISO 1167) have indicated that the performance exceed the minimum requirements for PE-100 pipe on hydrostatic strength. In addition, the predictive PENT (Pennsylvania Notched Tensile Test, ASTM F 1473) evaluation of the subject polymer indicate that the product will provide PE-100 and higher level of performance in pressure pipe across a broad range of MI, FI and density conditions. Table 3 provides evidence of this capability for the two products reported in Figure 5.

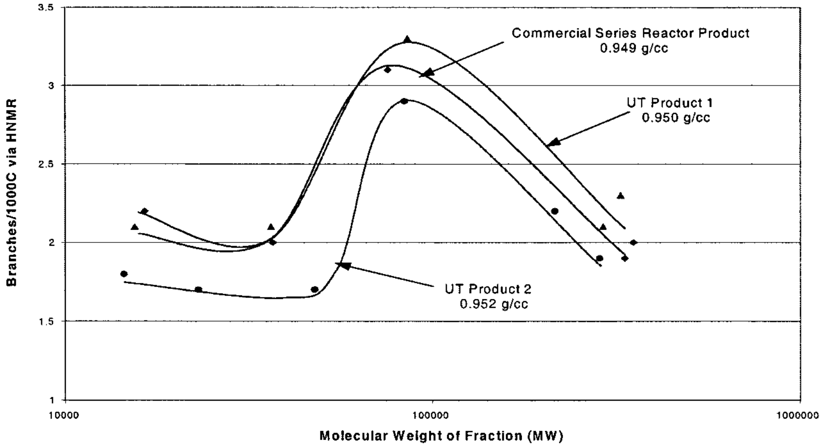

Figure 5. Reverse Comonomer Distribution for Engineered Caalyst Bimodal Samples vs. Commercial Series Reactor HDPE Product.

Table 3. Univation Bimodal PE-100 Pipe Product Capability Using Engineered Catalyst.

HMW-HDPE Product	Predictive Criteria for PE-100	UTEC Product 1	UTEC Product 2	UTEC Product 3
Resin Properties				
Melt Index, I_2		0.051	0.075	0.040
Flow Index, I_{21}		6.7	9.4	7.9
Melt Flow Ratio, I_{21}/I_2		133	125	200
Density, g/cc		0.950	0.952	0.949
PENT, hours @3.0 Mpa, 80 C	> 150	1896	320	2000+
Pipe Test Data		Bench-Top	Bench-Top	Hydrostatic Strength 32 mm SDR 11 pipe
Failure Time, hr @ 20 C, 12.4 MPa	>100	PENT only	PENT only	222
Failure Time, hr @ 80 C, 5.5 MPa	>165	Not Tested	Not Tested	643
Failure Time, hr @ 80 C, 5.5 MPa	>1000	on Pipe	on Pipe	1368+

Conclusion

Engineered Catalyst technology from Univation allows for the production of bimodal composition distribution and bimodal molecular weight distribution in a single gas-phase reactor. Through the proper combination of catalyst chemistry and advanced reactor controls, the technology delivers the capability to provide a wide range of tailored LLDPE and HDPE polymers in a single reactor.

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