Bimodal Polyethylene —
Interplay of Catalyst and Process

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SUMMARY: HDPE specialities having tailored bimodal molecular mass distributions suitable for applications as e.g. pipe or film material are formed in the Hostalen®-BM low pressure slurry process. A cascade of two STHD (stirred tank heavy diluent) reactors is used to produce at extremely different reaction conditions in each step of the polymerization an in situ polyethylene blend consisting of a low molecular mass homopolymer and a high molecular mass copolymer. This way, a resin having a very broad molecular mass distribution and an inverse comonomer distribution is obtained. High impact strength, stress crack resistance, stiffness, tensile strength, and good processability are combined and materials showing outstanding properties are achieved.

Introduction

The properties of polyolefins depend mainly on the polymer structure. For instance, the rather simple monomer ethylene can be converted into a great variety of polymer grades showing completely different mechanical properties suitable for many applications.
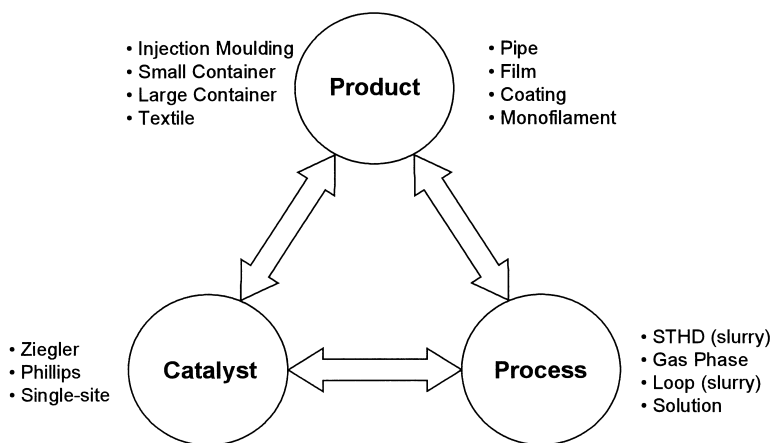

Fig. 1: Catalysts and processes for the production of polyethylenes.

Much is known about the structure-property-relationship of polyethylene and numerous polymerization technologies have been developed in order to tailor the polymer architecture of polyethylene[1] (Fig. 1). In such a technology both parts, the process and the catalyst, have to form a well-balanced system[2]. The catalyst is crucial for the polymerization reaction. By the cooperation of process and catalyst a definite polymer structure is produced.

Tailor-made bimodal molecular mass distribution

On principle, there are two ways to form polyethylene showing a bimodal molecular mass distribution (BMMD) (Fig. 2).
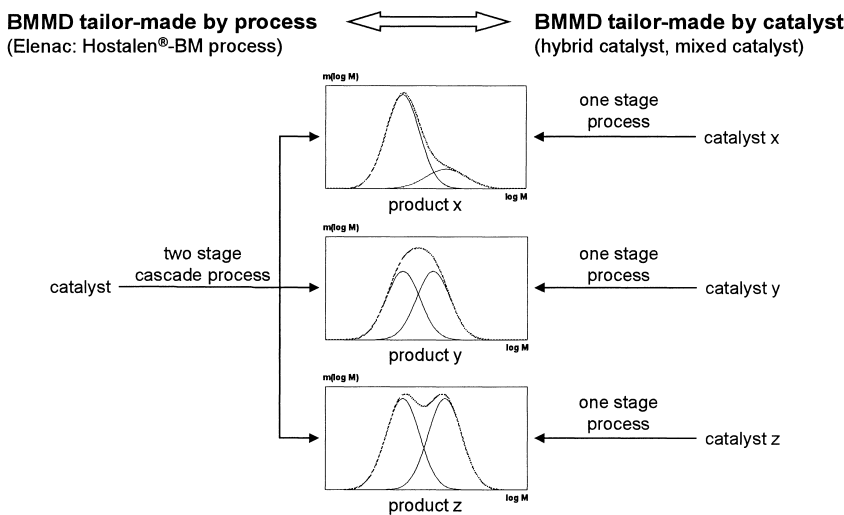

Fig. 2: Two ways towards bimodal polyethylenes.

One way is to synthesize a tailor-made catalyst. Hybrid catalysts or mixed catalysts unifying the properties of different active sites on each catalyst particle[3] can be used to obtain an in situ polyethylene reactor blend in a one stage process. For each bimodal grade a sophisticated catalyst has to be developed in order to adjust the amount, the molecular mass distribution, the comonomer incorporation, and the comonomer distribution of both fractions formed in the polymerization reaction.

Another way towards bimodal polyethylene in situ blends is to use a two stage cascade polymerization process. The catalyst passes two reaction zones and one polymer fraction is formed after the other at different reaction conditions. Only one optimized catalyst is required

for the production of various grades. The desired molecular mass distribution and comonomer distribution are designed by the process. Beside these features this technology offers further advantages: No change of the catalyst or cocatalyst is necessary when the grade is switched. Change is done by adjusting the reaction conditions whilst the space-time-yield remains constant. Thus, little time is required to pass on to the next grade and the amount of offspec material produced during the switch is nearly negligible. Starting from the catalyst feed and ending with the pelletized final product the cascade process can be designed as one continuously working production line.

STHD cascade process

The concept of a two stage cascade process is for instance realized in Elenac's Hostalen®-BM low pressure slurry technology. The core of this continuous polymerization process consists of two stirred tanks in series. Only one highly sophisticated 3rd generation Ziegler catalyst is used to produce all bimodal grades (Fig. 3).

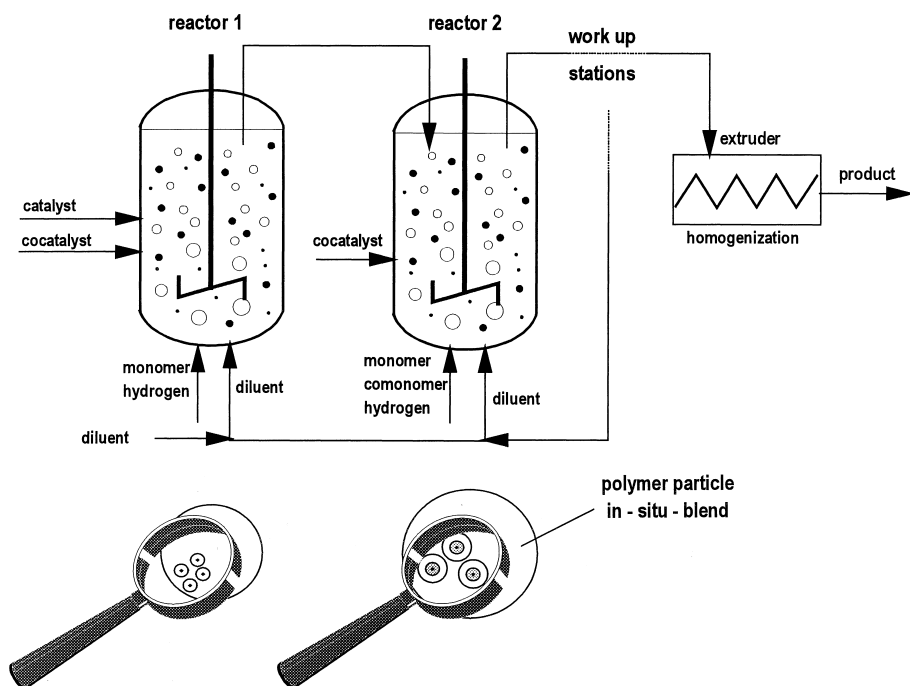Fig. 3: Elenac's Hostalen®-BM low pressure slurry process.

In the first reactor a very low molecular mass ethylene homopolymer is formed. The catalyst, cocatalyst, ethylene, and diluent (e.g. hexane) are continuously fed to reactor 1. The molecular mass of this polymer fraction is adjusted by adding an appropriate amount of hydrogen. Then the slurry is transferred into reactor 2 where the polymer particles with the still active catalyst polymerize under completely different reaction conditions and comonomer is added. A very high molecular mass copolymer is produced in this second stage. The polymer slurry is then passed to the working up station. The polymer powder is separated, dried, compounded and pelletized. The diluent is recycled after purification.

Every particle of the polymer powder produced in the cascade process has the same average composition. In the particle forming process[4, 5] each catalyst particle has to have the same activity and every volume increment has to contain the same number of active sites. Thus, the growth of the particles during the polymerization results in polymer grains showing evenly distributed layers of low molecular mass homopolymer and high molecular mass copolymer around the catalyst fragments[1] (Fig. 3 and Fig. 4).
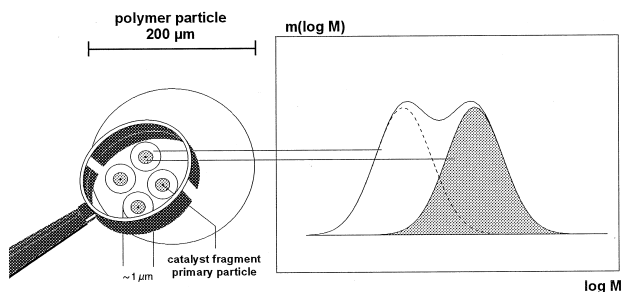

Fig. 4: Polymer particle structure of an in situ polyethylene blend produced by a cascade process.

This way, an in situ polyethylene blend is obtained. Such a high performance polymer alloy shows an outstanding combination of desired properties for e.g. pipe and film applications. The mechanical data measured (e.g. stress crack resistance, impact strength) are superior to those that can be achieved with conventional blends.

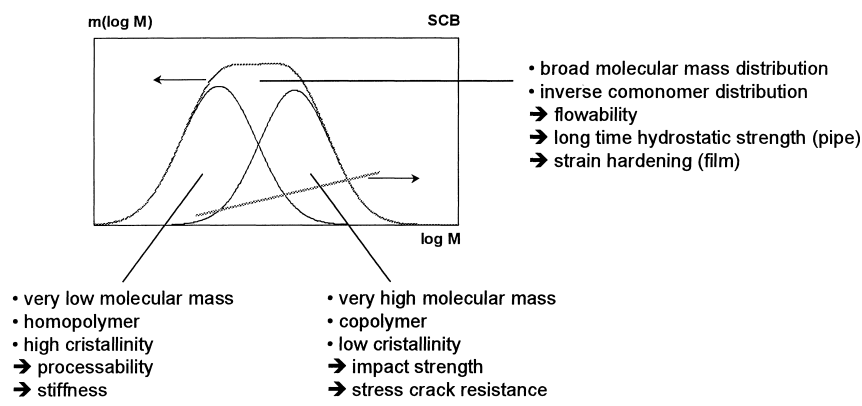# Structure-property-relationship of bimodal polyethylene

Fig. 5: Structure-property-relationship of bimodal polyethylene.

By the synthesis of bimodal polyethylenes the mechanical properties of the low molecular mass fraction and the high molecular mass fraction are combined (Fig. 5). This allows to produce materials showing higher stiffness, higher toughness, improved impact strength, higher stress crack resistance, and optimized processability compared to unimodal resins. The inverse comonomer distribution (Fig. 6 and Fig. 7) results in products with longer lifetime under stress[6, 7, 8, 9].
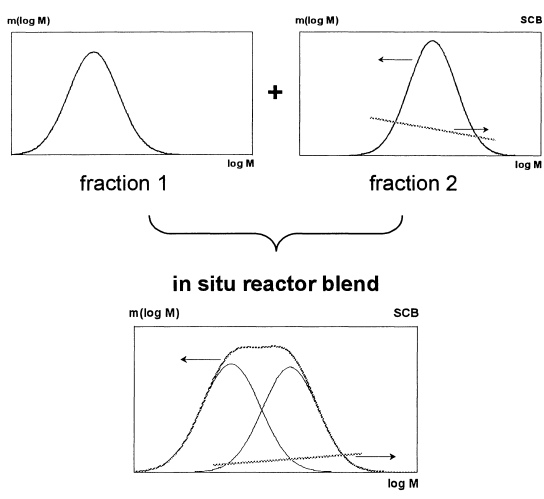

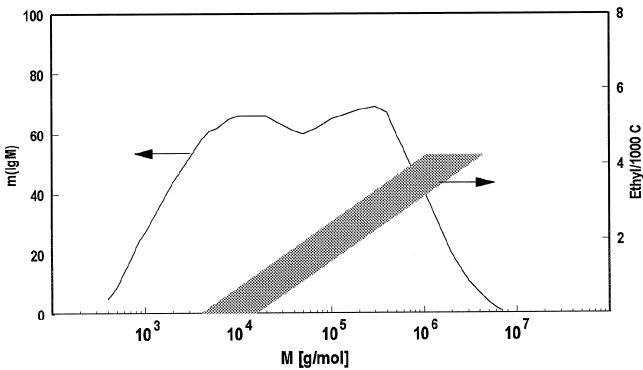Fig. 6: Inverse comonomer distribution of an in situ reactor blend.

Fig. 7: Molecular mass distribution (SEC) and comonomer distribution (Holtrup fractionation, FT-IR analysis) of a bimodal PE 100 pipe material.

Due to the fact that the comonomer is mainly incorporated into the long polymer chains bimodal polyethylene has a higher density compared to an unimodal polyethylene showing the same amount of short chain branches but no inverse comonomer distribution (Fig. 8). For that reason, bimodal polyethylene grades exhibit higher stiffness and enhanced stress crack resistance[10].
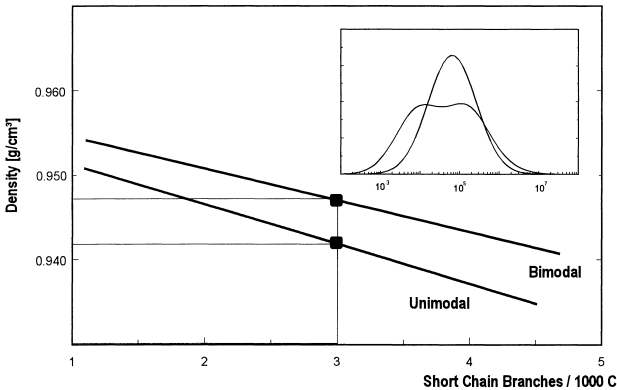

Fig. 8: Density of unimodal and bimodal polyethylene as a function of short chain branches.

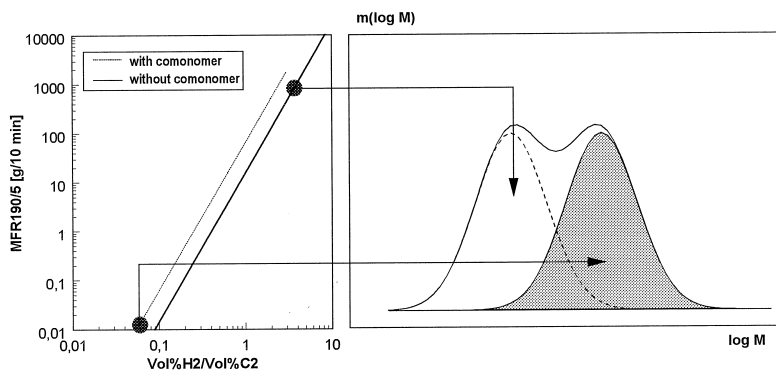# Catalysts optimized for the STHD cascade process

Fig. 9: Molecular mass as a function of hydrogen and comonomer concentration in a cascade process using an unimodal catalyst tailor-made for the production of bimodal polyethylene.

When the growing catalyst particles in the slurry pass through the reactor cascade they are subjected to extremely different reaction conditions. The molecular mass of the two fractions is controlled by the concentration of hydrogen within the vessel. Therefore, the catalyst has to show an excellent hydrogen response (Fig. 9) to reduce the amount of hydrogen required for molecular mass regulation because hydrogen decreases the activity of the catalyst[1].
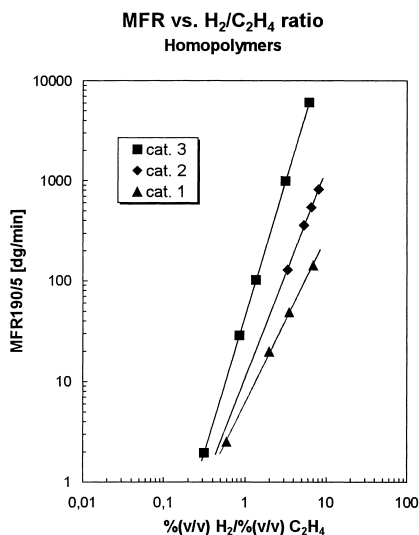

Fig. 10: Optimization of the catalyst with regard to hydrogen response.

The catalyst has further to be optimized with regard to the broadness of the molecular mass distribution and the comonomer distribution of the polymer produced. Also, the copolymerization behavior (Fig. 9) and the comonomer incorporation rate (Fig. 6) has to be to taken into consideration. As well, the catalyst has to show a very high productivity and activity in the polymerization reaction. Finally, to tailor products by the process a detailed knowledge about the temperature dependence of all these parameters is required.

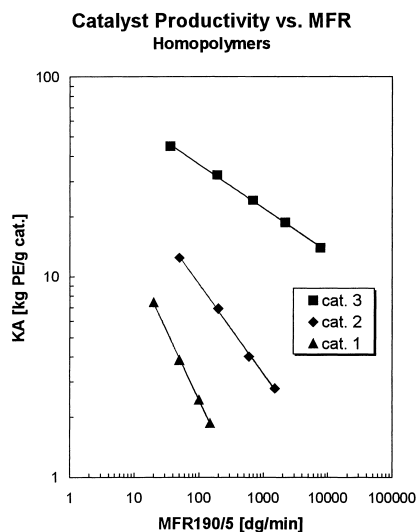**Catalyst Productivity vs. MFR**
Homopolymers

Fig. 11: Catalyst productivity as a function of melt flow rate.

In the particle forming process every polymer grain originates from one catalyst particle. Provided that no fragmentation of the catalyst particles into smaller sub-particles occurs during the polymerization and that every catalyst particle has the same productivity and activity the catalyst and the polymer powder show the same broadness of the particle size distribution[4, 5].

Ziegler catalysts are most suitable for Elenac's Hostalen®-BM low pressure slurry process. Highly sophisticated Ziegler catalysts of the 3rd generation supported on $MgCl_2$ have been developed. Fig. 10 and Fig. 11 show the improvement of the catalyst with respect to the hydrogen response and the productivity. Polymer powders having a high bulk density and a narrow particle size distribution are obtained. The catalyst shows an excellent hydrogen response in combination with high activity and productivity and is capable of forming a homogeneous comonomer distribution.

By the combination of this optimized catalyst and the cascade slurry process products with bimodal molecular mass distribution exhibiting outstanding properties are obtained.

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