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METOCENE TECHNOLOGY—AN OUTSTANDING TOOL FOR IMPROVING AND DESIGNING POLYPROPYLENE PROPERTY PROFILES

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ABSTRACT

Metallocenes are now well known as advanced catalyst components for the polymerization of olefins. At the beginning of this decade, high-performance metallocenes capable of producing polypropylenes with high molecular weight and high isotacticity were discovered.

The presentation is outlining the capability of Targor's Metocene Technology to generate new and improved polypropylene products for market applications. It is also describing the current status of Metocene commercialization by describing property profiles of various Metocene grades.

In injection molding, for example, Metocene's unique balance of transparency and modulus enables it to replace both crystal and impact polystyrenes in a wide range of thin-wall packaging application. In the textile sector, its beneficial properties make it a suitable candidate for producing high-strength filaments, fibers and extremely fine spun-bonded fleeces. Cast film applications offer very good optical and barrier properties at high processing speeds.

INTRODUCTION

Since then, continual research and development at Targor and its parent companies, BASF and HOECHST, in both the technological and product application field, has led to regular production of metallocene based polypropylenes and to a strongly increasing market demand for such products [1-4]. Targor, BASF, and Hoechst have combined considerable know-how and technological assets in the area of metallocenes and polypropylene, creating ideal conditions for further leading the scale-up and commercialization of metallocene polypropylene in Europe. Metocene is Targor's trade name for metallocene-based polypropylene and will also be used for labeling the related products and services such as Metocene Technology, Metocene Catalysts and Metocene Chemicals (Figure 1) [2].

Metallocenes are now well known in industry. What has not been discussed so far in much detail is the fact that metallocene technology is adding a new technological dimension to the existing technological basis for polypropylene. This new dimension takes the form of additional tools that can improve or replace existing technological variables for designing and/or improving PP properties.

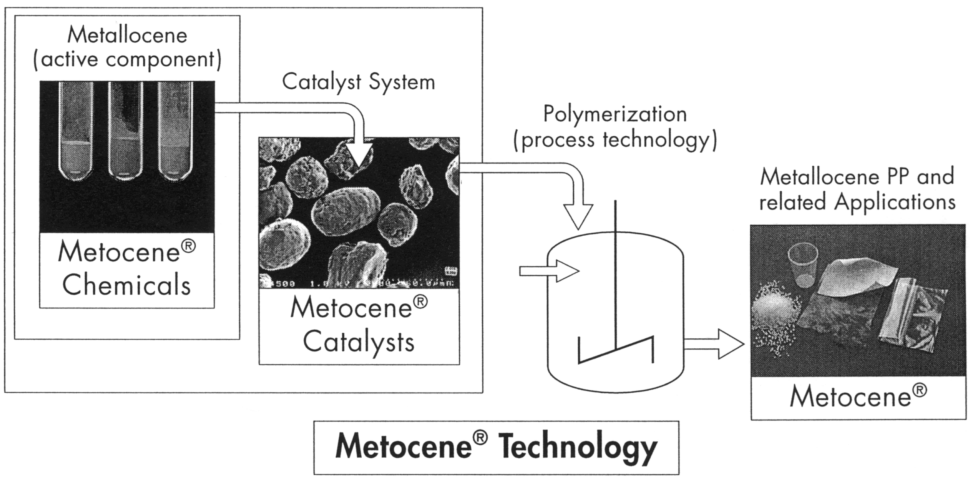

Figure 1. Targor's Metocene® Products.

The following very much aims to inform about Targor's recent progress in the development and commercialization of metallocene polypropylene.

Metocene Technology

Basic Characteristics and Variables

Although metallocene-related R&D is nowadays very much spread across the various steps of the value chain, it is still metallocene compounds that define the basis for improvements and innovation in catalyst, process and product development. Metallocene compounds, since they are the active species in the catalyst, set the frame for product and process performance in any metallocene-based technology. The most important feature of metallocene compounds are (Figure 2):

- the single-site character of single metallocene catalysts and
- the structural variability of metallocenes and corresponding performance characteristics.

These features lead both to uniform products with distinct characteristics and to a wide variety of products and property profiles [2]. Some distinct characteristics attributable to the single-site nature of single metallocene catalysts are [1, 3] (Figure 3):

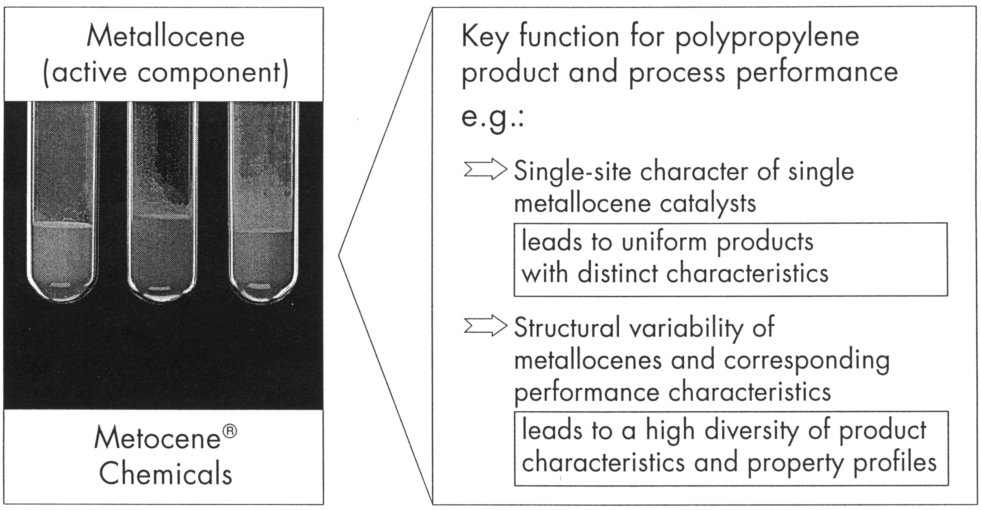

Figure 2. Basic Characteristics and Variables.

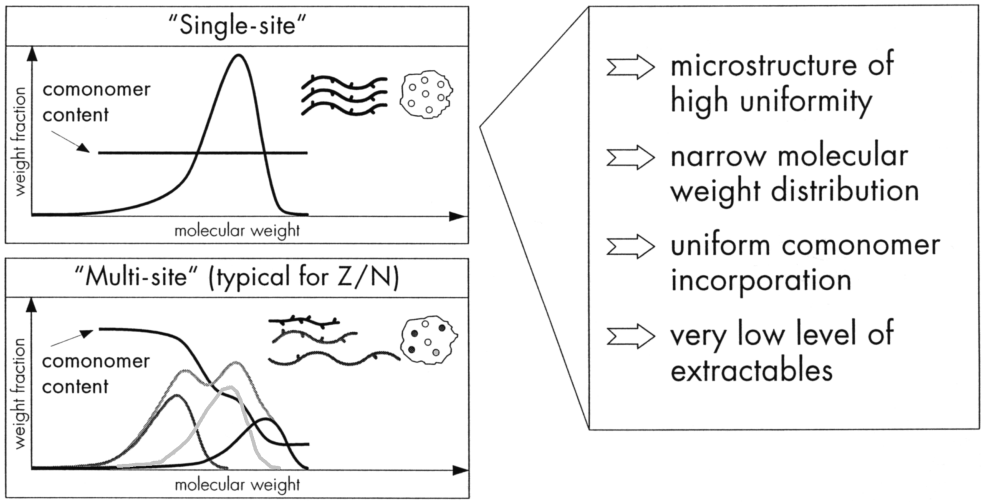

Figure 3. Single-Site Character in Single Metallocene Catalysts.

- uniform microstructure,
- narrow molecular weight distribution,
- uniform comonomer incorporation,
- low level of extractables.

The low level of extractables, in particular, is a general quality characteristic of metallocene-based products. It applies to polypropylene copolymers as well and it considerably extends the application range of all metallocene-based polypropylenes (Figure 4).

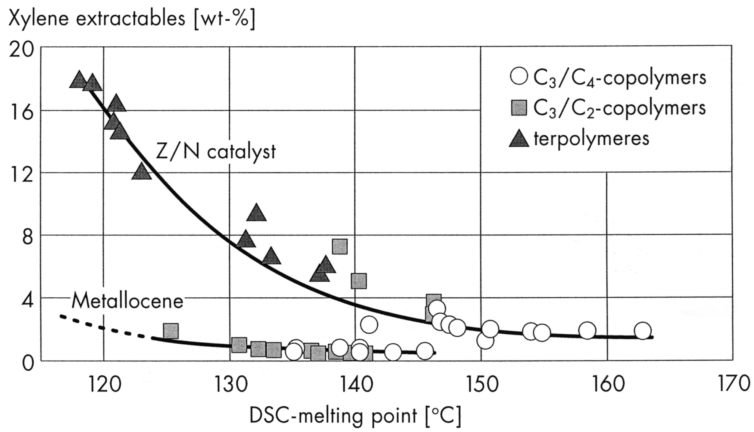

Figure 4. Low Level of Extractables.

With regard to the structural variability of metallocene compounds, a large number of structural variants of metallocenes suitable for the manufacture of polypropylene have already been identified. By careful metallocene selection, various microstructures, molecular weight ranges, hydrogen responses, comonomer incorporation rates, etc. can be chosen. As a result, a wide variety of property profiles are accessible by metallocene variation. Manufacturing conditions such as comonomer concentration, hydrogen concentration, polymerization temperature, etc. will also be affected by such changes in the metallocene.

Figure 5 is gives an indication of what is meant by the structural variability of metallocenes useful in PP manufacture. Figure 6 refers to metallocenes of the indenyl type and gives a general indication of the performance differences in iPP polymerization that result from different metallocene structures. It is evident that, in terms of molecular weight and melting point, this metallocene selection offers a broad basis for accessing the technical relevant iPP product range various polymerization conditions. If we also consider the options of combining two or more different metallocenes for manufacturing one PP product, the possibilities for product design are additionally enhanced.

The New Dimension

All the characteristics and variables mentioned so far represent new technological tools with broad application in the manufacture of new and improved

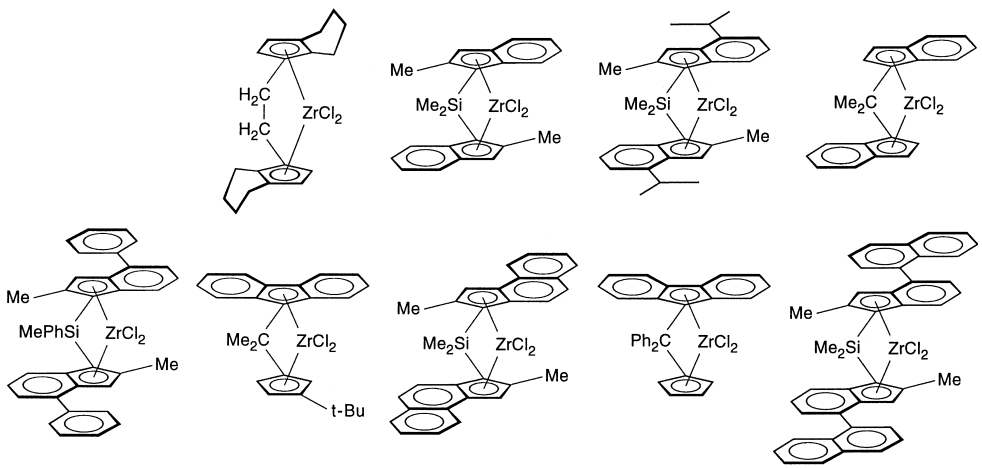

Figure 5. Structural Variability of Metallocenes (a).

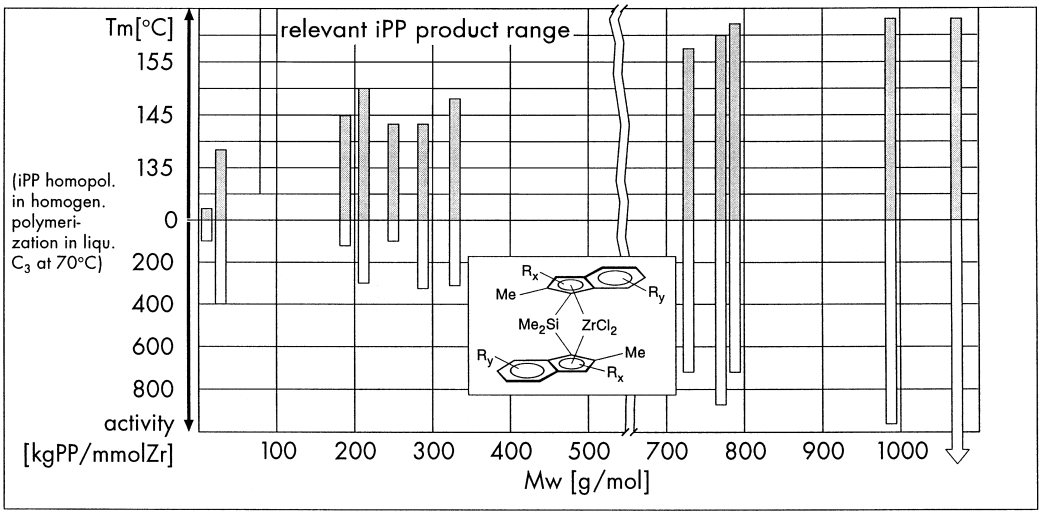

Figure 6. Structural Variability of Metallocenes (b).

products. If all such metallocene based contributions to product design are considered in combination with conventional technologies, a very new and broad field for technological design work is evident (Figure 7). Product designers can exploit both the unique advantage of catalyst variation offered by the metal-

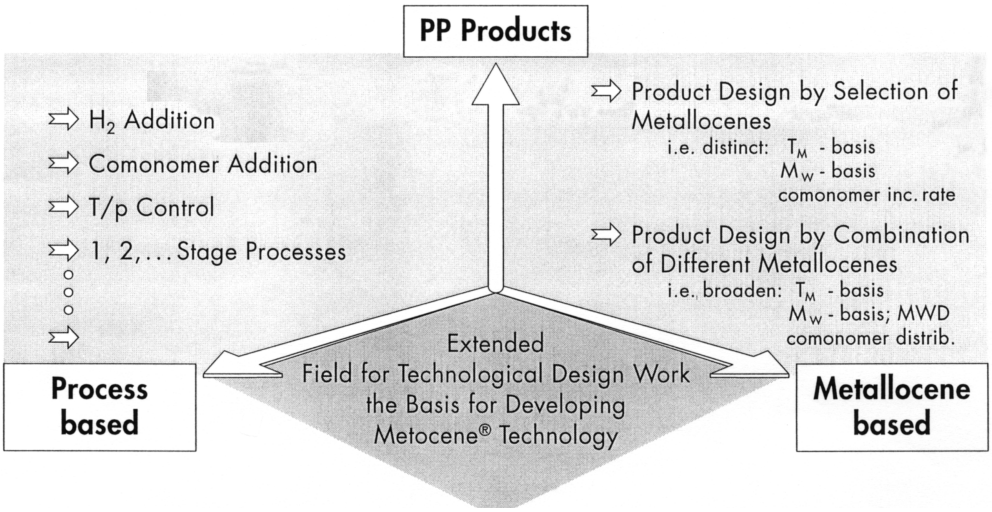

Figure 7. The New Technological Dimension (PP Products)

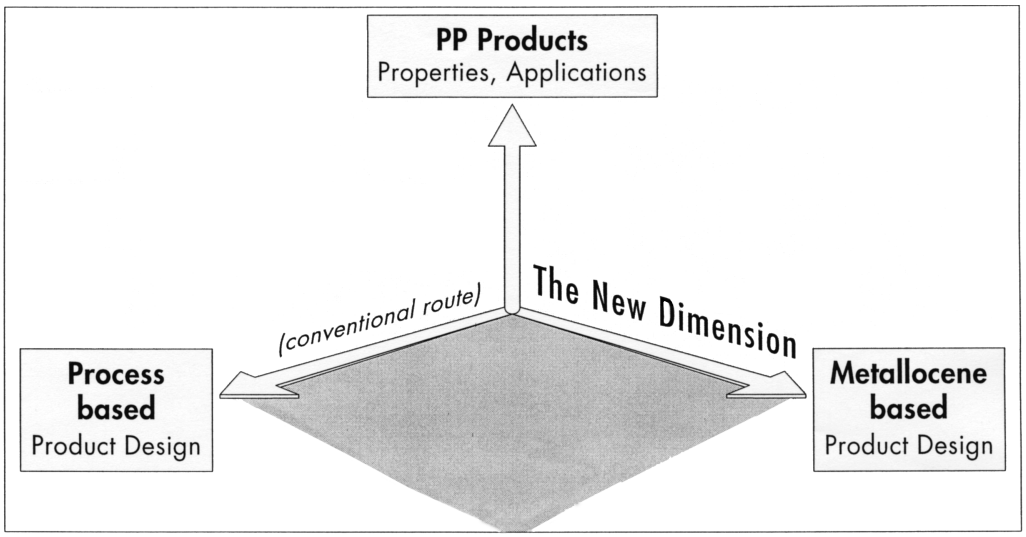

Figure 8. The New Technological Dimension (PP Products, Properties and Applications).

locenes and conventional options for changing process conditions to achieve new or improved properties. This field of technological design work forms the basis for Targor's Metocene Technology. Experience so far indicates that even if process complexity is reduced by metallocene catalysts the conventional process variability remains important.

So Metocene Technology is a technological tool that is adding new possibilities to established PP technologies [5]. In developing this catalyst technology in fact a new technological dimension is being exploited (Figure 8). In the following some information regarding Metocenes and market responses to them are presented. Although this is still the first phase of commercialization there is already enough reliable feedback from the market to confirm that metallocenes indeed open up a new technological dimension.

Metocene: PP Development and Commercialization

Injection Molding

About one year ago, Targor announced the launch of two high-melt-flow grades as commercial products. These were Metocene X 50081 and Metocene X

50109. The main target market is that of transparent packaging. Very promising applications involving replacement of polystyrene or polycarbonate have been identified [4]. In the field of random copolymers and blockcopolymers the product development is actually being performed in pilot scale and will not be further discussed here. Experience with Metocene X 50081 and X 50109 in transparent packaging confirms that the basic property advantages in this market sector are inherent features of Metocene Technology. They are:

- a unique balance of transparency and stiffness
- excellent contact transparency
- very good melt flow behavior
- outstanding organoleptic properties

Due to the uniform microstructure of the polymer, which produces a finer crystal structure, the transparency measured (according to ASTM D 10003) on a 1 mm sample is 93%. In the same test, polystyrene shows 98% transparency. In contact transparency, there is virtually no difference from polystyrene. Certainly, there are also other more general PP advantages in packaging that need to be reconsidered, as Metocene's transparency opens up new markets for polypropylene. There is, for example, the low density of 0.905 kg/liter, which together with Metocene properties previously mentioned is attracting considerable market interest. Some applications highlighted here can demonstrate this. Firstly, the broad field of polystyrene replacement is a large market, which includes both food packaging and technical packaging; then there is polycarbonate replacement and last but not least Metocene is being used instead of other transparent plastics, particularly in Germany, to reduce recycling charges (Dual System). Figure 9 shows in more detail the main advantages a customer can gain using Metocene instead of polystyrene for the same application. First of all, it is possible to downgauge by up to 30% because of Metocene's toughness versus polystyrene's brittleness; other advantages include lower melt temperature, reduced cycle time, no loss due to brittle fracture during assembly and, finally, large savings through overall weight reduction by up to 40% in the same application.

In transparent applications Metocene also has a functional advantage over the relatively brittle polystyrenes. Figure 10 shows a typical example. It is a transparent CD-ROM case of totally new design, which could only be produced as a result of Metocene's outstanding combination of transparency, stiffness and toughness. The CD case consists of at least two parts joined by integral film hinges and a CD removal mechanism. It is obvious that such hinges as well as the CD removal lever require high toughness. In the disposable or one-way packaging sector, Metocene offers an additional advantage over other transpar-

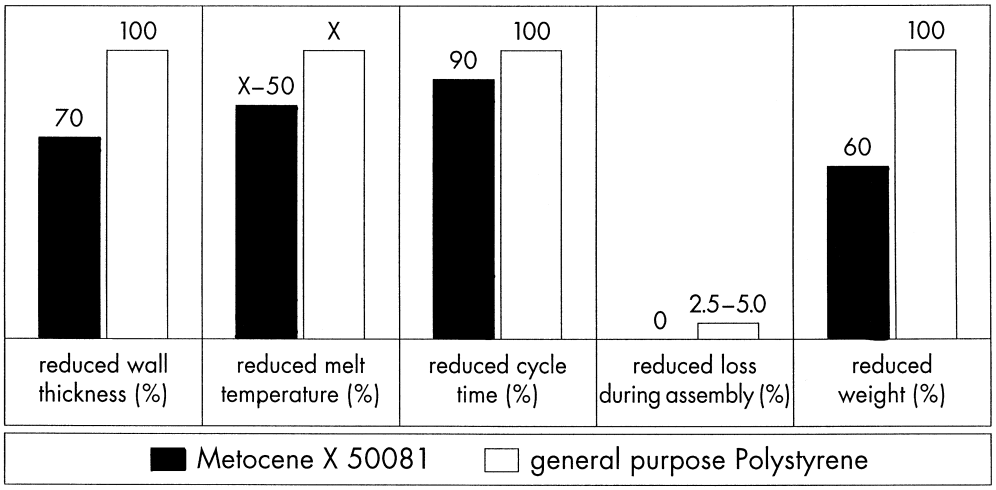

Figure 9. Substitution of Polystyrene in Technical Packaging.

ent plastics in Germany because of reduced "Green Dot" (recycling) charges (Figure 11). In the case of polystyrene replacement the advantage is 0.43 DM/liter. In polycarbonate replacement, the saving is even greater. The density advantage over polycarbonate is about 25% and the overall raw material cost advantage comes close to 80%. For polycarbonate replacement in houshold applications, such an advantage is a serious argument in favor of Metocene.

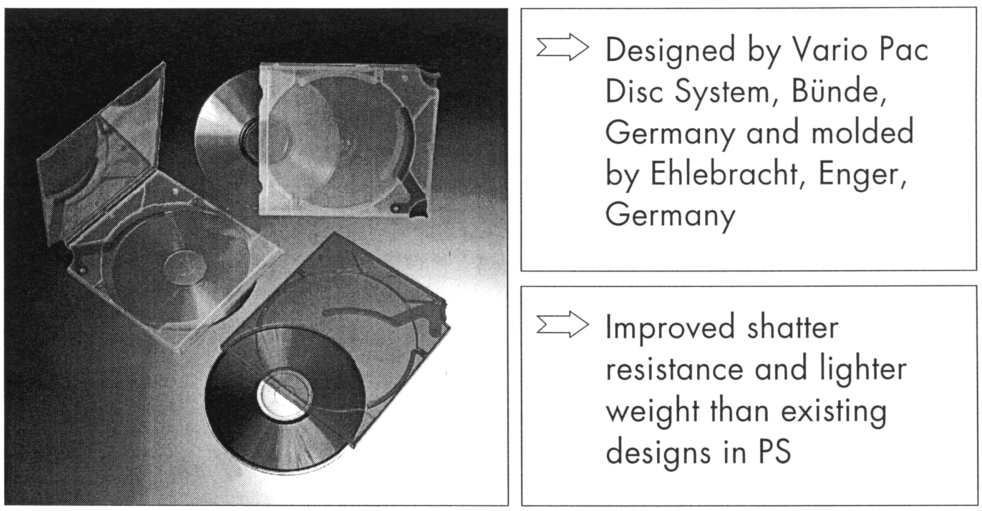

Figure 10. CD-ROM Packaging in Metocene X 50081.

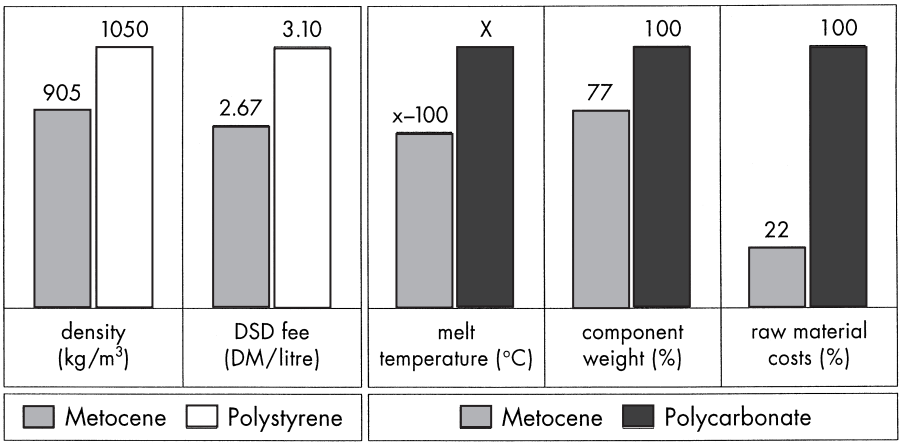

Figure 11. Reduction of DSD Fees/Polystyrene; Replacement of Polycarbonate.

Extrusion

In a phase of market development, experience has been gained in applications such as cast film, carpet fibers, staple fibers, nonwovens and melt blown products. The Metocene grades employed so far in these applications have been homopolymers withi MFR values ranging from 12 to 2500. Other Metocene extrusion products such as random copolymers or BOPP grades are currently in pilot scale development.

In cast film, the excellent optical properties of Metocene, especially at high processing speed, are among the most outstanding features identified. Many other advantages in terms of barrier properties, metallizability, blocking behavior, organoleptic properties and last but not least sealability add up to a very attractive property profile in comparison with conventional PP grades. The sealability (Figure 12) of Metocene-based cast film is comparable with that of conventional random copolymers. It is believed that Metocene can offer a unique property profile in this application. In terms of sealing properties and optics, the profile is comparable with that of conventional random copolymers, while with regard to stiffness the profile is closer to that of conventional PP homopolymers.

In filaments and fibers, it is mainly the low elongational viscosity, high melt stretchability and high polymer orientation of Metocene that lead to higher tenacity fibres or the possibility of spinning very thin fibers. The narrow molecular weight distribution of this PP and excellent molecular weight control make

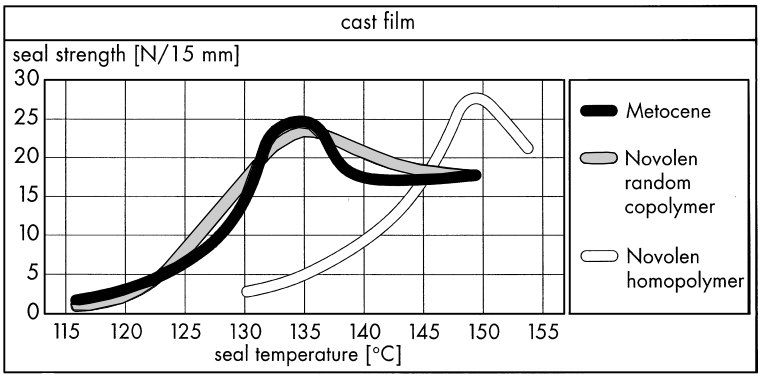

Figure 12. Excellent Sealability (cast film).

it possible to manufacture super-high-flow polymers directly from the reactor. Such Metocenes are very clean and uniform products as they are not affected by any conventional post-reactor visbreaking and show excellent properties in melt blown applications.

In textile applications, two achievements need to be highlighted, one involving directly spun POY (partially oriented yarn) and another from relating to needle-felts (Figure 13). In the case of directly spun POY yarn, we have been able to achieve a 100% tenacity increase. This has strengthened the confidence to target as well polyester replacement in the future market development. In geo-textiles, Metocene offers a combination of 15% improved tenacity and very good

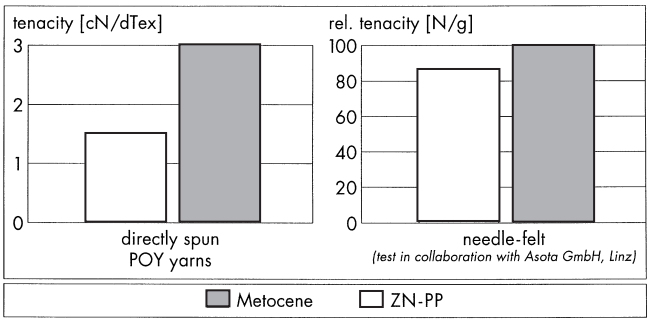

Figure 13. Filaments/Fibers.

elongation behavior. Again Metocene is setting new standards in such applications. Other applications which should be mentioned here are nonwovens, where very good processibility in terms of spin stability and throughput is being achieved, and where reduced titers, even below 1 dtex, are being attained. The access to fine-titer filaments is leading up basic improvements in the manufacture and use of fleeces for hygiene applications. The end-use profile of these fine-titer-based fleece is characterised by even coverage, good appearance, improved barrier properties, high tenacity, and an outstandingly soft feel.

A final example is Metocene in melt blown and spun-bonded composites (Figure 14). Here again, the ability to generate very fine titers is leading to improvements in terms of fine pore size and permeability behavior and is also opening up new applications. The combination of increased water barrier effect and high air permeability is extremely valuable in this application. Metocene provides this property!

CONCLUSION

To conclude on a more general note, it is reasonable to state that the examples presented here demonstrate that metallocene polypropylene is pushing back the limits of polypropylene application and is about to set new standards in various markets and applications. In particular, one can conclude:

All market and application feed back strongly indicates that in fiber, cast film and transparent injection molding applications, lasting advantages of metallocene based PP have been secured.

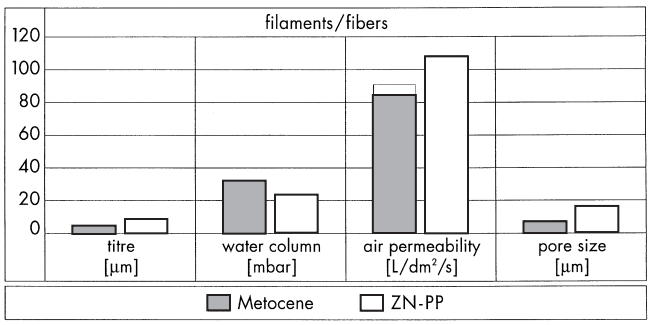

Figure 14. Melt Blown (filament/fibers).

Metallocene based PP not only offers property improvements in existing PP applications, but also opens up new applications and markets with high value creation. This will accelerate the substitution-based growth of polypropylene.

Given the positive market response to METOCENE and looking into the future, it seems evident that full participation in future market growth will hardly be possible without access to metallocene based polypropylene.

ACKNOWLEDGMENT

The Metocene-related development and commercialization activities involve various teams working at or for Targor. All the participants in these activities and especially the team members are gratefully acknowledged.

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