

## Polypropylene Used In Injection Molding





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# About LyondellBasell Industries



LyondellBasell Industries is one of the world's largest polymers, petrochemicals and fuels companies. We are the global leader in polyolefins technology, production and marketing; a pioneer in propylene oxide and derivatives; and a significant producer of fuels and refined products, including bio-fuels.

Headquartered in The Netherlands, LyondellBasell has combined annual revenues of nearly \$45 billion and approximately 17,000 employees worldwide. Our vertically integrated facilities, broad product portfolio, manufacturing flexibility, superior technology base and reputation for operational excellence allow us to deliver exceptional value to our customers across the petrochemical chain – from refining through to advanced product applications.

LyondellBasell is dedicated to ongoing research and development programs that meet the ever-changing requirements of our diverse customers, including the creation of new catalysts, processes and products. Our materials are used in virtually every market to manufacture countless goods and products that enhance quality of life for people around the world.

At LyondellBasell, we clearly recognize the importance of being a responsible corporate citizen in our communities. We are committed to operating our businesses with the highest principles of integrity, ethics and corporate responsibility, as well as the highest standards of health, safety and environmental performance.

LyondellBasell products are the basic elements used to manufacture countless goods and products that people use every day. From fresh food packaging, clean fuels and durable textiles to medical applications, construction materials and automotive parts, the uses for LyondellBasell materials are almost unlimited.

# About this brochure

This brochure is intended as a guide on the use of LyondellBasell's polypropylene resins used in the injection molding market. It has been written and produced to help LyondellBasell's customers become more familiar with these resins, and to enhance their understanding of the way in which these resins interface with the injection molding process. The brochure is aimed at LyondellBasell's customers throughout Europe.



LyondellBasell operates sophisticated and advanced manufacturing technologies at various sites throughout Europe. These include *Spheripol*, which, through LyondellBasell's licensing activities, is the most widely-used process in the world for the production of homopolymers, heterophasic copolymers and random copolymers. The company also produces resins using other gas and liquid-phase processes, and by its new and revolutionary *Spherizone* polypropylene process. Furthermore, as a leader in catalyst development, LyondellBasell routinely manufactures polypropylene using either the industry-standard Ziegler-Natta catalysts or its leading-edge metallocene catalysts.

LyondellBasell's polypropylene exhibits a wide range of physical properties, and are used by customers in many different molding applications. Consequently, the materials must be clearly differentiated, one from another, and so, as shown in Table 1, LyondellBasell has allocated a number of different trade names. All of them are polypropylene, but needless to say, with very different properties from each other.

Trade-name	Characteristics
<i>Moplen</i>	Regular homopolymers, heterophasic copolymers and random copolymers
<i>Adstif</i>	Ultra-high crystallinity grades
<i>Clyrell</i>	Impact resistant, transparent grades
<i>Metocene</i>	Ultra-high clarity homopolymers, heterophasic copolymers and random copolymers, produced using metallocene catalysts
<i>Purell</i>	Specialised materials used in healthcare applications
<i>Stretchene</i>	Transparent polypropylene used for the production of clear bottles by injection stretch blow molding

Table 1: LyondellBasell's trade-names for polypropylenes

The key factors involved in the overall molding train are shown diagrammatically in Figure 1. It is absolutely essential that those persons responsible for specifying the end-use performance of a molded polypropylene item not only understand the importance of each individual part, but also that they appreciate that many parts are inter-related, and so may need to be considered both separately and jointly.

Each of these factors is discussed in detail in forthcoming parts of the brochure (with the exception of economics which is a highly specialized subject and completely outside the scope of this work). By way of introduction it provides an analysis of the markets in which molded polypropylene has been established, together with a brief description of the requisite performance requirements. This is followed by more detailed information on the different types of polypropylene developed and marketed by LyondellBasell (and as introduced in the above table), and then the bulk of the brochure concentrates on the actual molding of polypropylene – namely, the conversion equipment and the conversion technology. The brochure also provides information on ecological matters, and on material form and availability.

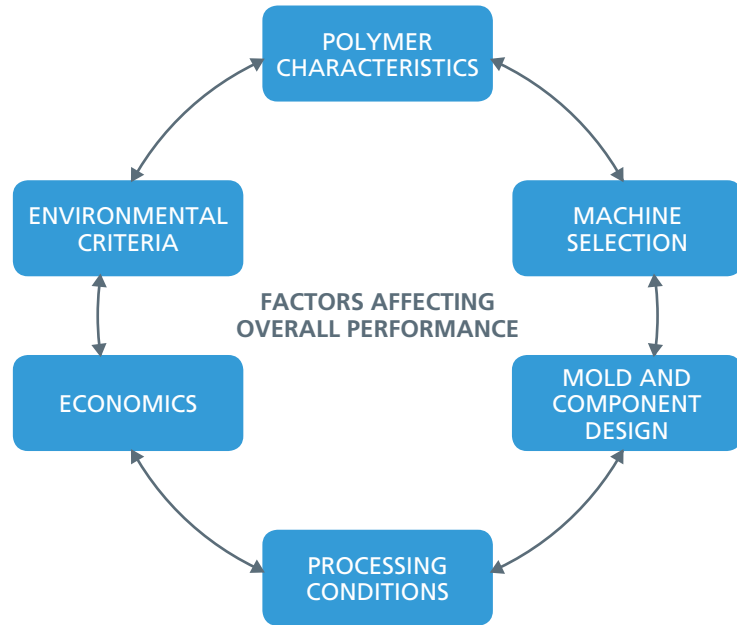


Figure 1: Factors affecting the overall moulding train

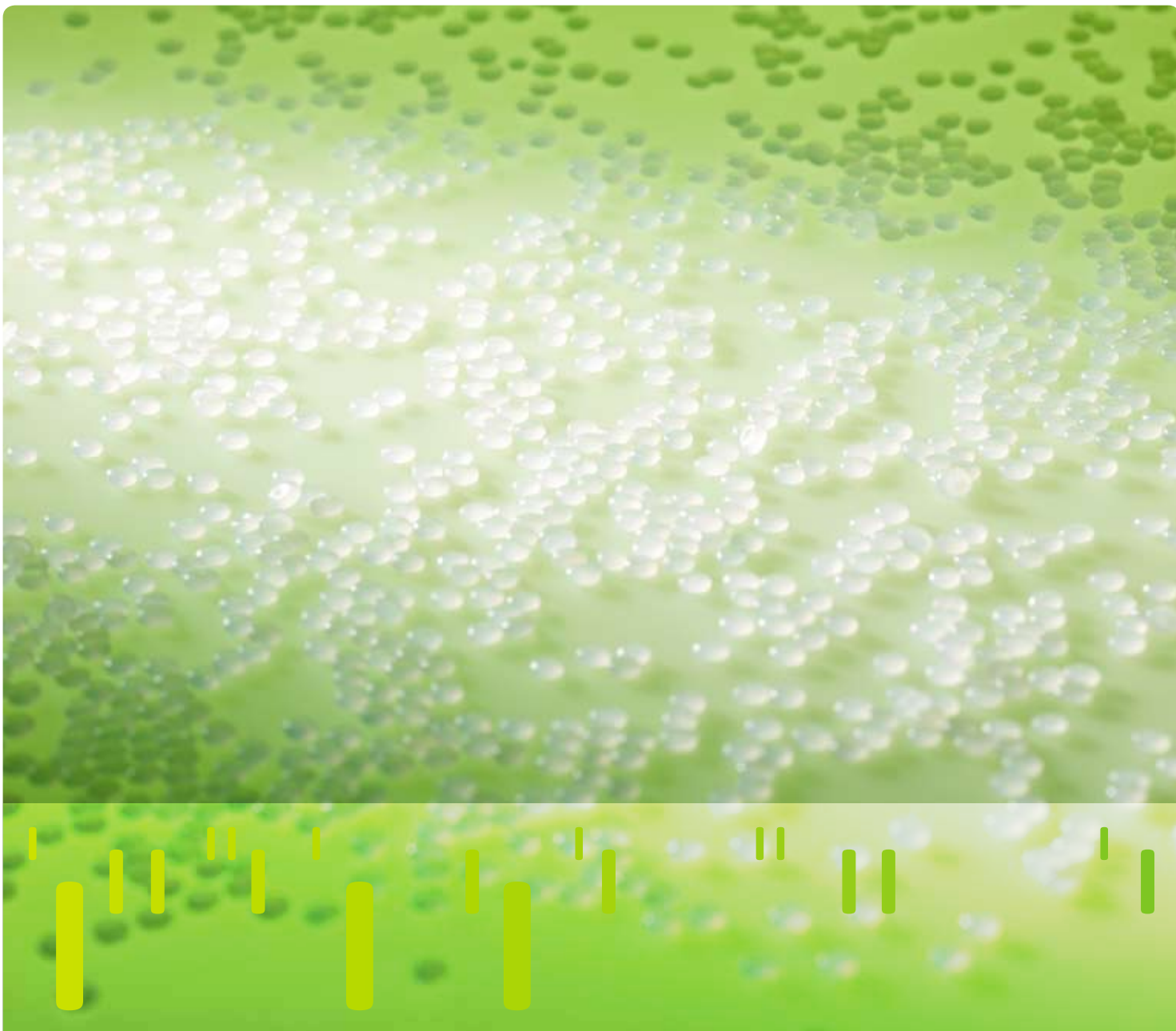
Finally, in order to properly do justice to a subject of this type, there is inevitably a need for a certain amount of background information – in this instance specifically concerning the structure, manufacture and properties of polypropylene. However, since additional facts of this type can easily lead to the brochure becoming unwieldy, this important information has been moved to the end of the brochure, where it is presented in the form of a Background note.

Customers, end-users and other readers of this brochure should be aware that any information submitted here reflects LyondellBasell's current knowledge and experience, which is based on its own expertise, activities and feedback from customers in regions where the company is present. It does not therefore

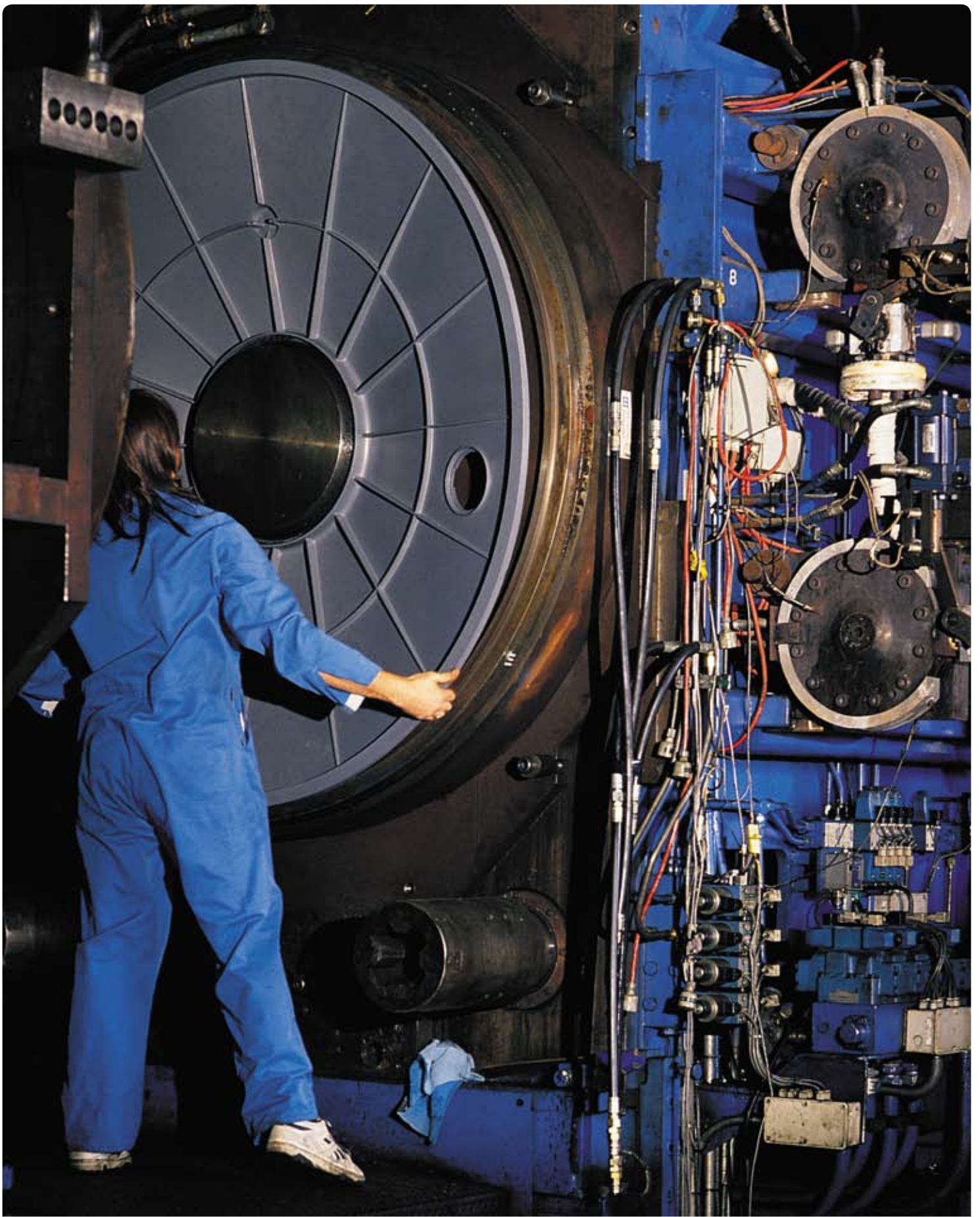
represent a comprehensive assessment by LyondellBasell of the materials and conversion process in question in every regional market.

This brochure contains no information on individual grades. This is intentional, as the document has been written for LyondellBasell's customers throughout Europe. Inevitably, individual grade types will tend to vary, reflecting local needs from market to market, and therefore grade-specific examples, while helpful to one customer, could be misleading to another. Comprehensive information on individual grades is of course available, and can be obtained directly from LyondellBasell's local technical and sales staff.

As LyondellBasell cannot anticipate all conditions under which its polypropylene may be used, as such or in combination with other products or materials, nor can LyondellBasell anticipate the many factors that may affect storage, use, processing, installation, application, shelf-life and service life of such materials and related products, the information contained in this brochure should be considered as preliminary and general nature, and not treated as a substitute for specialist advice and assistance.



Before using a LyondellBasell polypropylene, or selecting an injection molding conversion technique or otherwise using a LyondellBasell product for a specific application, customers and other users should conduct their own tests and experiments, and make their own independent determination that the product is suitable for their intended use and applications. They should also ensure that they can use the LyondellBasell product safely and legally – “Material Safety Data Sheets” (also known as MSDSs) are available from LyondellBasell. Furthermore, a listing of compliances in accordance with the requirements laid-down by various regulatory bodies is provided in what are called “Regulatory Affairs Product Stewardship Information/Certification Data Sheets” (also known as RAPIDS). Copies of both documents may be obtained on-line, at [www.polymers.lyondellbasell.com](http://www.polymers.lyondellbasell.com).





# Market analysis and performance requirements

This section of the brochure provides a listing of the major applications in which molded polypropylene is used, together with a brief review of selected performance requirements.

Injection molding is one of the most widely-used conversion processes in the entire European market, and its versatility has led to it being used for the manufacture of an extremely diverse range of goods. Equally, polypropylene is one of the most widely-used thermoplastics in this same market, and in turn, its versatility has led to it being used for the manufacture of an equally diverse range of goods.

The combination of polypropylene and injection molding has led to the establishment of a truly astonishing range of different applications, as detailed below.

LyondellBasell offers a full range of different types and grades of polypropylene used in each and every one of the listed applications, and further information on these materials is provided later in this brochure [*See: Forward to LyondellBasell's polypropylene portfolio*].

## Rigid packaging/hollow containers

LyondellBasell's polypropylene resins have a proven track-record for use in the production of molded rigid packaging and hollow containers. The market is dominated by the packaging of food, but the market for other applications such as the packaging of emulsion paint is also important.

A brief description of the rigid packaging market is provided below, but more detailed information on both this and on the different types of polypropylenes offered by LyondellBasell is available in a separate brochure entitled **"Polypropylene used in rigid packaging"**, copies of which can also be obtained from local sales and technical centres, and on-line at [www.polymers.lyondellbasell.com](http://www.polymers.lyondellbasell.com).

## I Food Packaging

The principal foods packaged in molded polypropylene containers are dairy goods such as cream, yogurt, yellow fats, and ice creams, together with soups, certain “microwavable-only” meals, and dehydrated commodities like pot noodles. Container wall sections are generally rather thin, and flow-paths to thickness ratios of the order of 300:1 are not uncommon.



Most molded containers in this sector of the market are likely to be produced at high operating speeds, and this modus operandi necessitates the use of special types and grades of polypropylene. A list of typical requirements that such a material must satisfy are shown in Table 2.

Table 2: A selection of material requirements to be satisfied during the production of thin-walled containers.

- I Exhibit a suitably low melt viscosity to satisfy the needs of high-speed mold filling
- I Exhibit re-crystallization characteristics commensurate with the need to solidify within the permitted cooling time – usually very short
- I Be sufficiently rigid to resist any tendency to distortion during ejection
- I Be thermally stable
- I Suffer from no deterioration of its organoleptic characteristics
- I Exhibit consistent and reproducible shrinkage characteristics, in accordance with specified and agreed tolerances
- I Exhibit a level of resistance to distortion and warpage commensurate with the needs of the application

LyondellBasell is well aware of these conversion-related performance requirements, and so those of its *Moplen* homopolymer, random copolymer and heterophasic copolymer polypropylene resins used in this area of the market have been designed with these requirements in mind.

Moving to the performance of the containers during end-use, the overwhelming requirement here is the provision of safe physical protection for the packaged goods – during storage by the packer-filler, during transit to the retailer, and during storage and use by the end-user. This requirement is manifest in a number of different ways, but usually includes a need to provide adequate top-load strength, to protect against accidental damage due to impact abuse, and to be resistant to the chemical nature of the packaged contents.

In addition to these general requirements food packaging brings with it a further list, much of which is essential and non-negotiable. Examples include:

- All containers, together with the polypropylene resins from which they were made, must fully satisfy a comprehensive list of national and international regulations concerning contact with food
- Throughout their service life they must fully protect against oxidation and product deterioration during the recognised service life
- Similarly, they must fully protect against ingress of moisture
- Similarly they must also fully protect against micro-biological attack
- The polypropylene packaging shall not impart any taint, odor or off-flavor to the food
- Where and when applicable, the packaging should be resistant to high temperatures
- The protection against accidental damage mentioned above should, where and when necessary include exposure to low and sub-zero temperatures.

Once again, LyondellBasell is well aware of these important additional requirements, and once again those of its *Moplen* polypropylene resins used in this market have been designed accordingly.

## I Packaging for emulsion paint

The packaging of industrial goods such as emulsion paint usually necessitates the production of up to four separate components – the can, the top rim into which the lid will recess and fit, a molded handle and the lid itself.



Modern emulsion paint cans are essentially straight-sided (in other words with absolutely minimal draw-taper), and components of this type place quite stringent demands on the design of the ejection facilities in the mold, and on the de-molding part of the conversion process. From a material standpoint the conversion requirements are rather similar to those associated with the production of thin-walled food containers – although the organoleptic characteristics are no longer as important.

In complete contrast to the requirements for thin-walled food containers however, paint containers must be able to withstand potentially rough handling during use. While they should never normally be exposed to low temperatures, the cans still have to be able to demonstrate a very high level of physical strength overall. They need to be robust enough to withstand repeated opening and closing. Furthermore, they need to be able to withstand accidental impact abuse, and to demonstrate excellent creep resistance in order to handle the weight of a stack of full cans.

On at least two counts the material used for the production of the rim of the can must exhibit excellent dimensional stability – on the one hand the rims are often attached to the tops of the cans by a secondary process of spin welding, and on the other there must be a liquid-tight fit between the rim and the container, and the rim and the lid.

The conversion requirements associated with the production of the lids are discussed separately under the section on caps and closures.

## I “Stand-alone” containers

The market for injection molded “stand-alone” containers” is relatively small in comparison to the one for food packaging, and arguably the most significant part is that for plant pots.



## Caps and closures

Most of the hollow containers discussed above, together with other packaging items such as bottles, jars and tubes are going to need some kind of closure in order to provide safe and reliable packaging. This market is one of the largest within the overall molded polypropylene area. It is also extremely diverse, and is routinely used by industries such as beverage, wine, beer, food, cosmetics, personal hygiene, paint and more.

A brief description of the rigid packaging market is provided below, but more detailed information on both this and on the different types of polypropylenes offered by LyondellBasell is available in a separate brochure entitled **"Polypropylene used in rigid packaging"**, copies of which can also be obtained from local sales and technical centres, and on-line at [www.polymers.lyondellbasell.com](http://www.polymers.lyondellbasell.com).

The production and use of beverage closures forms the largest part of this particular market, and this sector is reviewed below. In addition, there are many smaller segments, and a selection of the more interesting ones is also discussed.

More comprehensive details on this important sector of the overall market are provided in a separate brochure entitled "Polyolefins used in caps and closures", copies of which may be obtained from local sales offices and technical centers, and online at [www.polymers.lyondellbasell.com](http://www.polymers.lyondellbasell.com).

### I Beverage closures

Beverage closures are typical of the "screwed-on" variety, in which an internal thread engages with a similar one molded into the neck of the bottle or container. Polypropylene is widely established for the production of the injection molded two-piece variety, the closures being used typically with carbonated soft drinks and with juices.

The polypropylene must exhibit consistent and reproducible shrinkage characteristics during molding. This high level of dimensional consistency is required because of the rigorous demands established in performance specifications and subsequently encountered during end-use. Furthermore, the thread must not be damaged or distorted during ejection, even though it effectively forms a continuous undercut, necessitating the closure to be stripped or "jumped"

from the mold during ejection. Consequently at the temperature of ejection the polypropylene must also exhibit an appropriate balance of rigidity and elasticity in order to resist the forces encountered. In addition, there must be no damage to the tamper-evident feature.

Further information on the subject of undercuts is provided later-on in this brochure [See: **Conversion equipment – Component design – Undercuts**].

By any yardstick, the end-use performance requirements placed upon beverage closures are exceptionally demanding. Many of the major beverage manufacturers set their own specifications, and a typical test protocol may well include application and removal tests, gas venting testing, abuse testing and organoleptic testing among many others.

Almost all beverage closures incorporate a tamper-evident feature. Most feature a band that must rupture cleanly at the point or points of attachment to the closure when the latter starts to be unscrewed. The separation must be in a brittle fashion, and it must never occur prematurely. One of the material properties controlling this particular performance requirement is known as notch sensitivity, more information on which is provided later in the Background note on the structure and properties of polypropylene.

The use of LyondellBasell's *Moplen* polypropylene resins in the manufacture of beverage closures has been established over many years. They offer easy molding characteristics, good impact strength, resistance to doming, and are generally accepted as being stress-crack free.

## I Closures incorporating secondary features

In overall tonnage terms the market size for closures incorporating secondary features is much smaller, but on the other hand such closures exhibit significantly more variation of design and application.

Secondary features perform an additional task, over and above that of the basic closures to which there are attached. Many different varieties are available, and some of the more common ones are reviewed below – child-resistance and hinges. With its easy molding characteristics and its high level of shear sensitivity polypropylene is particularly suited to this type of closure.

Child-resistant features are designed to prevent young and inquisitive children from gaining access to potentially hazardous materials. Their removal from a bottle or a container usually requires more than one action, coordinated at the same time. In some markets approval for use is only granted provided that the closure satisfies a test panel comprising both children and adults.

A number of different variants are routinely available. Most consist of two parts, and in addition some closures feature a combination of child resistance and tamper evidence.

Moving on, the use of closures that incorporate a hinge is widespread, and this particular feature is an excellent example of the added convenience that such attributes can bring.

The design and location of the hinge are extremely important, and not only affect its performance but among other things they also exert a major influence on the transmission of pressure through the melted polymer. This subject is also discussed in greater detail later in the brochure [See: *Conversion equipment – Component design – Hinges*].

Finally, many closures incorporate more than one secondary feature, an excellent example of which can be seen in a modern pump closure. This is arguably one of the most sophisticated combinations of secondary features encountered in the market. LyondellBasell's *Moplen* polypropylene resins have an excellent track-record in applications of this type.

## I Flat lids for paint cans

The overriding performance requirement for lids used as part of the packaging for liquid and semi-liquid products is the provision of a leak-proof seal with the container or can.

However, unlike screwed-on closures there is no provision for the application of torque, and so their performance is largely dependant on dimensional integrity of both the lid and the rim, and the compression/elastic properties of the polypropylene used for their production. These requirements are made all the more demanding by the fact that the lids will almost certainly be center-gated, and have virtually no side-walls. Consequently, it is extremely important that the selected grade exhibits reproducible shrinkage characteristics and a high level of resistance to distortion.

In addition to this stringent requirement, the selected polypropylene must also be able to withstand repeated opening and closing. And finally, for reasons of convenience, many converters prefer to produce both the can and the lid from the same grade of polypropylene.

LyondellBasell is well aware of these demanding requirements, and is none the less able to offer materials that can be considered for these kinds of applications.



## Consumer products

The market for consumer products, while lacking the sheer size of the one for rigid packaging, none the less encompasses an extremely wide range of interesting and demanding applications, for the most part quite different from each other.

Consumer products may be conveniently described as being “articles used in daily life”. They are largely “ready-to-use” items in which the durability of the material is an essential property.

### I Battery cases

The use of molded polypropylene has been established over many years, particularly for automotive starter batteries (under the bonnet/hood).

During conversion the candidate polypropylene must exhibit good dimensional stability, and in particular a low warpage or distortion to the internal separators. In addition, since most battery cases are first of all molded in two parts which are subsequently welded together, the polypropylene must also exhibit good welding characteristics.

Most batteries are heavy, and consequently there is a risk of robust handling during installation and removal. It follows therefore that the grade of polypropylene from which they are made must exhibit a suitably high level of resistance to abuse, even at low temperatures. All batteries tend to become warm when operating, and in particular starter batteries are regularly exposed to elevated temperatures, and so the candidate material must exhibit an excellent thermal stability – including an absolute minimum of heat-induced after shrinkage. Furthermore, aesthetic faults such as stress-whitening are completely unacceptable, particularly so because many batteries contain a dark-colored pigment. Finally, in view of the acidic nature of the electrolyte the battery case must also exhibit excellent chemical resistance and no environmental stress cracking.

LyondellBasell manufactures a range of polypropylene resins used in battery cases, covering most major applications. They exhibit good dimensional and thermal stability, high impact resistance and good weld characteristics.

### I Chairs and furniture

Polypropylene resins are routinely used for the production of molded chairs and furniture in both indoor and outdoor applications. Uses include the likes of stadium seats and garden furniture on the one hand and chair shells for domestic and office use on the other.

Most injection molded chair and furniture applications involve the production of relatively large components, necessitating the use of equipment and technology quite different to that employed with rigid packaging. Historically the use of polypropylene has been established for decades, and the performance requirements, while not particularly wide-ranging, they do have a number of essential components. All chairs must exhibit a balance of flexibility for comfort and strength/rigidity for support, although in respect of the latter component design also plays an important role [See: *Conversion equipment – Mold and component design – Ribs and bosses*]. In addition indoor chairs are likely to have at least one embossed surface, and so the material must be able to accurately reproduce such a pattern, some of which are very complex.

To a large degree similar requirements also apply to stadium seats, but with the added provisos that they must be able to withstand even more robust handling, and they must incorporate a UV stabiliser

in order to protect the polypropylene against degradation by sunlight and also to ensure minimal colour change over the service life of the seat.

Over the years LyondellBasell has established an excellent track-record for the supply of polypropylene to this sector of the injection molding market. The company’s grades provide a balance of good mechanical performance coupled with easy processing characteristics.

Chairs and tables designed for use in the garden were traditionally made from quite complex blends of polypropylene resins, additionally containing filler such as calcium carbonate. However, not only did the use of such a system necessitate an additional processing step to incorporate the various blend components, the presence of the filler in the surface layers tended to gradually lead to the build-up of unsightly dirt on the surfaces. However, LyondellBasell’s high crystallinity *Adstif* heterophasic copolymers now offer what has been termed a “mono-solution” to this former problem.

Finally, in recent times certain innovative component trends have emerged, for example:

- Plastics coupled with metals such as aluminium for aesthetic “high-tech” appeal
- Surface finishing via the application of in-mold label technology
- Translucent effects





## I Crates and boxes

Crates and boxes are a further example of molded applications that have been established for decades, but more recently some interesting developments have reached the market.

The traditional polypropylene crate was originally a replacement for a metal version. It had to withstand exceptionally robust handling, and in particular impact resistance over a range of temperatures, excellent load-bearing properties and good creep-resistance. Crates tended to be relatively thick-walled and heavy, and the heterophasic copolymers from which they were produced had somewhat limited flow characteristics. While acceptable at that period of time, cycle times were relatively long and outputs relatively low. In addition problems of stress-whitening were common, and transparency unheard of.

Today, things are quite different. A new generation of heterophasic copolymers has been developed which exhibit the requisite balance of impact resistance and load-bearing, but at significantly higher fluidity, thereby permitting wall thicknesses to be reduced, component weight to be saved and outputs improved.

In addition to regular crates a new generation of lightweight foldable display boxes has also become established. These molded components have to be strong enough to withstand robust handling and storage in an agricultural/horticultural pooling environment, plus have fold-down sides to permit the produce to be displayed on arrival and to reduce the risk of strains and injury while it was being removed from within. In addition, they have to fold flat for storage and improved transport efficiency when empty.

LyondellBasell has been at the forefront of developments of polypropylene resins used in this sector of the market, and never more so than in the recently expanding area of transparent crates and boxes. Of particular noteworthiness are LyondellBasell's *Clyrell* polypropylene resins, which are becoming established for use by certain supermarkets, and LyondellBasell's *Metocene* resins that are used for the production of catering drawers by certain transport companies.

## I Housewares

Most housewares require superior aesthetic characteristics coupled with outstanding functionality, and these are demands that are ideally suited to the properties of polypropylene – across the board, and including most of the different types. Consequently, polypropylene is widely used for the production of a variety of houseware applications.

By way of example, *Moplen* homopolymers, random copolymers and heterophasic copolymers are used for the production of items such as home storage containers and kitchen ware, and high fluidity copolymers for thin-walled storage containers. In addition, random copolymers are regularly used tcontainers, and impact-resistant clear grades such as LyondellBasell's *Clyrell* resins are used in the production of clear containers intended for storage at lower temperatures.

## I Luggage

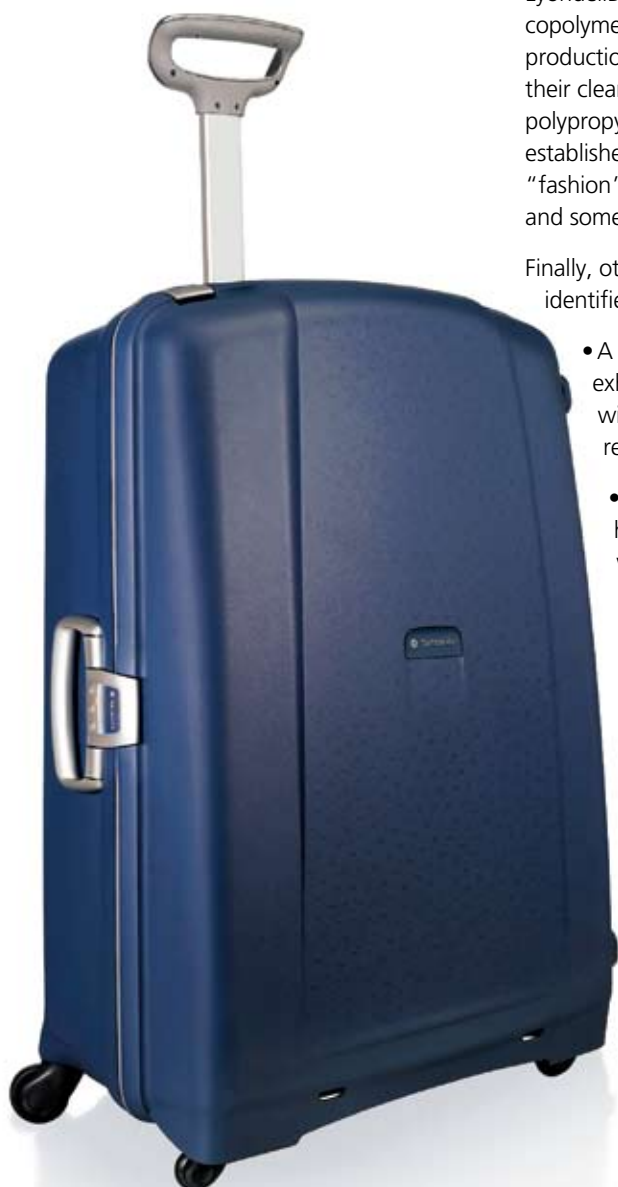
The performance requirements for a candidate polypropylene to be accepted for the production of rigid luggage bear some similarities to those for crates and boxes, in so far as it must exhibit an exceptionally high impact strength in order to withstand the sometimes rough handling at airports and the like, but at the same time the case must not be unduly heavy.

However, there is in addition an aesthetic dimension. Most rigid cases have a sophisticated embossed surface, and many contain a dark-colored pigment. Consequently, under no circumstances must they exhibit any stress-whitening or blushing.

LyondellBasell's *Moplen* heterophasic copolymers are regularly used for the production of suitcases. In addition, their clear, impact-resistant *Clyrell* polypropylene resins are becoming established for the production of "fashion" cases, often brightly colored and sometimes with a metallic surface.

Finally, other innovative trends identified in recent times are:

- A move to the use of materials exhibiting increased rigidity, but without any loss to the abuse resistance
- Similarly, a move to the use of high-flow polypropylenes, but without any compromise to the impact/rigidity balance
- Combination of the use of polypropylene and other materials in order to enhance still further the aesthetic characteristics



## I Toys, leisure and sporting goods

Lightness, optimum rigidity/impact balance and excellent gloss have made polypropylene an ideal material for the design and manufacture of a wide range of goods in this sector of the market.

LyondellBasell offers a wide range of *Moplen* heterophasic copolymers and random copolymers used in these applications, together with their special clear, impact-resistant *Clyrell* resins, and their *Adstif* high-rigidity resins. These materials have a proven track-record for the provision of robustness, non-toxicity, and a tremendous scope for the addition of vibrant colours.





## Multimedia and information technology

*Moplen* random copolymers and LyondellBasell's *Metocene* resins are being used for the manufacture of molded cases for DVDs and computer games in this ever-growing market.

Polypropylene resins of this type have been selected because of their outstanding aesthetic characteristics, such as clarity, gloss and "sparkle", which are generally considered to be consistent with the image of high-profile, "leading-edge" products with which this packaging is used. In addition, and in the case of the *Metocene* resins, their improved resistance to warpage and distortion is also advantageous.

## Other important injection moulding applications

Certain markets of strategic importance to LyondellBasell are outside the scope of a brochure of this type, namely, automotive and electrical, and healthcare products. However, in view of the importance in which they are held by LyondellBasell, a very brief introduction is provided below.

### I Automotive and electrical

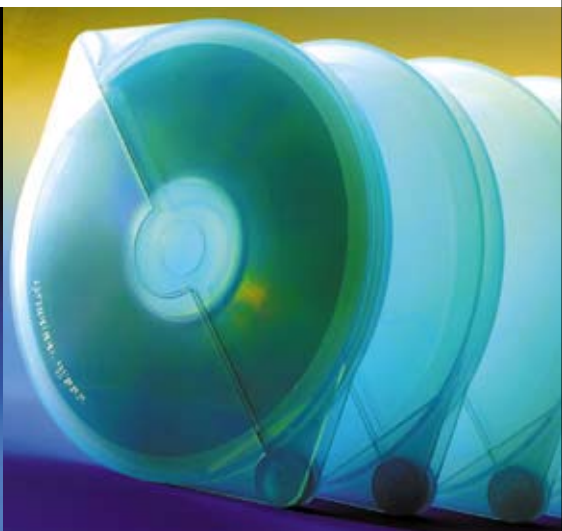
LyondellBasell is a world-renowned supplier of highly sophisticated and highly advanced polypropylene compounds used in injection molded automotive and electrical applications.

Further information on the markets for automotive and electrical goods, and on the performance requirements that must be satisfied can be obtained from a series of separate brochures, copies of which may can be obtained from local sales offices and technical centers, and online at [www.polymers.lyondellbasell.com](http://www.polymers.lyondellbasell.com).

### I Healthcare products

The performance requirements that must be satisfied when producing healthcare products tend to be highly specific to a given application, and, dependant on the nature of that application, extremely demanding. Furthermore, candidate materials must satisfy the requirements established by international pharmacopoeias.

Although outside the scope of this particular brochure further information on the market for healthcare products can be obtained from a separate publication entitled "Polyolefins used in healthcare applications", copies of which may be obtained from local sales and technical centers, and online at [www.polymers.lyondellbasell.com](http://www.polymers.lyondellbasell.com).





# Forward to LyondellBasell's polypropylene portfolio

LyondellBasell is the world's largest producer of polypropylene and has been closely involved with its development since one of its heritage companies (Montecatini) played a major role in its discovery in the 1950s.

The popularity of polypropylene is arguably related to its ready processability, its performance and its ecological acceptability, coupled with its cost and availability

LyondellBasell remains very much at the leading-edge of modern developments, both in terms of overall manufacturing technology and in terms of polypropylene used in the injection molding market. Consequently it is now able to routinely offer not just an impressive range of grades, but an impressive range of different production processes, with ranges of grades within each.

This part of the brochure provides a general introduction to the various types available from LyondellBasell. Furthermore, and largely for the benefit of those customers unfamiliar with polypropylene, a description of the structure, manufacture and properties is given in the Background note at the end of the brochure.

## The *Moplen* range

LyondellBasell produces *Moplen* grades used in many of the applications described earlier.

LyondellBasell's *Moplen* range of polypropylene resins is produced using modern variants of the Ziegler-Natta process, and encompasses the three basic types of polypropylene – namely homopolymers, heterophasic copolymers and random copolymers. These materials exhibit a very wide range of melt flow rates, and impact/rigidity balances, each one having properties commensurate with the needs of the market in which it is used. In addition, some are exceptionally clear while others exhibit high levels of gloss.

## *Adstif* ultra-high crystallinity grades

LyondellBasell has for some years been able to produce special polypropylene resins exhibiting a higher than usual level of crystallinity. Sold under the trade name *Adstif*, these grades exhibit very high rigidities, similar to those of some of the toughened polystyrenes and PVCs.

Components produced from these materials have demonstrated improved gloss and surface hardness, coupled with better resistance to high temperatures. They are available in homopolymer, heterophasic copolymer and random copolymer formats.

## *Clyrell* resins

LyondellBasell's *Clyrell* block copolymer resins provide a different balance of properties from that of other, more conventional polypropylene resins, and effectively bridge the performance gap between impact resistance and transparency.

With developments based on the original family of polypropylene resins, it was often difficult for manufacturers to make impact-resistant grades that also exhibited good transparency. Consequently, the packaging industry was faced with the dilemma of either sacrificing transparency for toughness, or vice versa.

LyondellBasell's *Clyrell* resins offer:

- Transparency
- High resistance to stress whitening
- Gloss similar to that exhibited by random copolymers
- Impact resistance typical of that for heterophasic copolymers – for some grades even at exceptionally low temperatures

In addition, certain grades achieve this remarkable balance at the same time as retaining a high level of rigidity.

*Clyrell* resins are routinely produced using either Ziegler-Natta technology or metallocene technology.

## Metocene polypropylene

LyondellBasell's advanced *Metocene* polypropylene resins, produced using leading-edge metallocene technology, are available as homopolymers, heterophasic copolymers and random copolymers. These materials exhibit a different balance of properties, and offer the prospect of extending the boundaries of acceptability for polypropylene used in many injection molding markets.

They are typically characterized by:

- Exceptional clarity
- Greatly extended melt flow rate range, without recourse to secondary processing
- Enhanced resistance to distortion and warpage
- Improved organoleptic properties
- Homopolymers exhibiting lower melting points

While all of LyondellBasell's *Metocene* polypropylene resins exhibit exceptional clarity, it is particularly noteworthy that the see-through characteristics of some grades are so good that they are being actively considered as alternatives to polycarbonates in the injection molding area.

## Other important polypropylene resins

As mentioned earlier, two important applications for injection molded polypropylene resins lie outside the scope of this brochure, namely automotive and electrical applications, and healthcare applications.

### | ***Hifax* and *Hostacom* compounds used in automotive and electrical grades**

LyondellBasell offers one of the most comprehensive ranges of polypropylene compounds available on the market. Grades specified and used by LyondellBasell's customers for exterior automotive applications are marketed under the trade name *Hifax*, while those for interior automotive parts, under the bonnet/hood compounds and electrical applications are sold as *Hostacom* grades.

Full details of the materials used in these applications may be obtained from local sales offices and technical centers, as explained earlier [*See: Market analysis and performance requirements – Other important injection molding applications*].

### | ***Purell* resins used in healthcare**

In recognition of the unique requirements that must be satisfied when candidate materials are used for the production of healthcare products, LyondellBasell decided that its polypropylene resins which can be considered for use in this area should be designated with the trade name *Purell*.

LyondellBasell is a committed supplier to this sector of the market. Its *Purell* polypropylene resins are routinely produced using either Ziegler-Natta technology or metallocene technology. Full details of the materials used in these applications may be obtained from local sales offices and technical centers, as explained earlier [*See: Market analysis and performance requirements – Other important injection molding applications*].

# Conversion equipment

The conversion equipment may be conveniently divided into the injection molding machine on the one hand and the mold on the other. In addition however, the design and shape of the component also exerts a major influence on the conversion equipment, and therefore needs to be given due consideration.



Machine selection, mold design and component design are complex subjects, a proper understanding of which requires considerable expertise and practical experience. It should be clearly understood that the remarks provided by LyondellBasell on these subjects are merely intended as a helpful introduction. They are not necessarily comprehensive, and should not be treated as a substitute for specialist advice. It is strongly recommended that the prospective converter always seeks such advice before any commitments are made.

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## Molding machine

This part of the brochure contains a summary of the basic features that may be considered when selecting equipment for use with polypropylene. However, the general principles are applicable to many moulding operations.

Molding machines are usually characterized by reference to the capacities of their plasticization unit and their locking unit. A large number of different types are available, although in most cases their manufacturers usually try to balance the

performance of the individual parts. In addition, some manufacturers offer the further possibility to choose individual units to suit specific requirements – for example, high-speed injection molding machines for the production of thin-walled rigid packaging.

As a general rule, a first approximation of the likely plasticization and locking requirements is often made by reference to the type, size and shape of the component or molding to be produced, and the numbers required.

### I Injection unit

The converter should ensure that the plasticization capacity of the injection unit matches the requirements of the component(s) to be produced.

The injection unit should be capable of providing a sufficient quantity of plasticized material within the conventional plasticization time. If the unit is too small then it may be necessary to extend the overall cycle time until plasticization has been completed – thereby reducing the output. In addition, material homogeneity may also start to be sacrificed. On the other hand, the use of an excessively large unit sometimes results in thermal degradation of the material due to excessively long residence times.

Many experienced converters will build in some small amount of extra capacity to accommodate any unforeseen additional demands in the future.

The use of shut-off nozzles allows plasticization to continue while the injection unit is retracted, and even during the application of back-pressure.

A screw cushion of between 3 and 12 mm of plasticizing stroke has been mentioned in literature, dependant on the screw diameter and the melt compression.

The potential plasticization capacity of the injection unit is usually described in terms of its swept volume and shot capacity/weight, and these parameters are in turn defined by the size/diameter of the barrel/cylinder and the screw. In a basic configuration such as a cold-runner system (either in total or in part) the swept volume and shot capacity must be greater than the combined weight or volume of the moulded components and their feed system. Generally speaking, the requisite shot weight would usually represent up to 75 - 85% of capacity.

The screw diameter should be selected according to the molding volume and the output required. From first principles the ideal length for polypropylene is longer than that for polystyrene, the depth in the feed zone greater and the compression ratio higher. In practice this means that the length/diameter ratio should be in excess of around 20/25:1, and the compression ratio around 3:1.

Finally, a non-return valve is usually located at the front of the screw, its function being to prevent the melt from flowing back into the screw flights during injection and the application of follow-up pressure. In addition, it is reported that a non-return valve is widely used when producing components in which minimum warpage and maximum dimensional stability have been specified.

### I Locking unit

The capacity of the locking unit may be defined as the force required to keep the two halves of the mold closed during injection and cooling. The degree of force is governed by the projected area of the component, the length of flow in the mold coupled with the wall-thickness through which the incoming material must travel, and by the injection pressure and injection rate required for smooth mold filling.

Generally speaking, a force of 4.0 kN/cm<sup>2</sup> of projected area has been reported as being adequate. However, because of the rather more extreme conditions of injection under which thin-walled containers are usually produced such components require a higher locking force.

Finally, components molded with a regular, single-face tool will normally require an opening stroke of more than twice their depth – examples would typically be larger items such as crates and boxes. On the other hand many much smaller items, for example caps and closures, are often made using a double-stack tool, and pro-rata to the length of the moulded component these will require an even greater opening stroke.

## Mold design

The importance of mold design and its influence on fundamental requirements such as shape, mechanical properties and appearance cannot be overstated.

### I General principles

A number of basic recommendations can be made. Some of these are applicable to almost all molding operations, irrespective of the raw material being processed, while others are more specific to polypropylene. Examples are provided in Table 3, followed below by further comments on selected items from the list.

Table 3: General and specific requirements for mould design

- I Provide an adequately dimensioned feed and runner system – this is a general requirement applicable to all moulding operations.

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- I Design the feed and runner systems so that melt accumulation and “dead spots” are avoided, and that material flow is smooth and even – another general requirement.

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- I Pay careful attention to both the design and the location of the gates – see further information below.

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- I Design the mold cooling system to ensure adequate and even cooling of all parts of the component – particularly applicable to the production of components with complex shapes, such as crates and boxes made from polypropylene - see further information below.

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- I Ensure that the metals from which the various parts of the mold are constructed are of suitable hardness – this is important in all molding operations, but is particularly relevant when high locking forces are being applied, typically during the production of polypropylene containers with thin side-walls and long flow-paths.

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- I Ensure that any individual core and cavity inserts are designed and located in such a way as to minimize deformation during mold filling – once again, this is relevant to all molding operations, but particularly so to the production of polypropylene containers with thin side-walls and long flow-paths.

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- I Select the type of ejection system to be used in accordance with the design and shape of the component to be produced – a general requirement.

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- I Provide suitably located and adequately dimensioned vents in order to facilitate trouble-free evacuation of air during mould filling – see further information below.

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- I Provide suitable tolerances to all dimensions in order to accommodate mould shrinkage – in addition, see “Component design”.

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- I Wherever possible avoid unnecessarily abrupt changes in cross-section, and in particular avoid all notches - in addition, see “Component design”.



## I Gates and runners

Careful attention should be paid to the design, layout and dimensions of the mould feed system. These are important considerations, and they affect the ease of mold filling, the control of dimensional tolerances and shrinkage, and the control of warpage and distortion.

In particular the gate(s) should ideally be located in such a way that it/they:

- Ensure a balanced flow of material into the mold, so that all areas of the component become evenly packed.
- As a general principle, feed into the thickest section of the component, thereby directing the flow essentially from thick to thinner sections.
- Ensure that the mold cavity may be filled under realistic conditions of temperature and pressure.
- Minimize weld lines as far as possible, or otherwise try to position them in non-critical areas of the component.
- Prevent jetting by positioning the gate in such a way as to introduce a controlled degree of turbulence to the flow of the material.
- Limit the possibility of air-entrapment.

As explained later in the brochure optimum control of shrinkage is obtained by carefully maintaining flow for as long as necessary during the application of the after pressure [See: *Conversion technology – Shrinkage*]. Although processing parameters such as the melt temperature play a major role in achieving this objective, the design and location of the gates is also important. In an ideal situation the best results would be obtained when using a large gate in which the material does not set-up too quickly. Furthermore, such a gate also permits easy mold filling, without the generation of high levels of shear and orientation. However, for small or thin-walled components fed by a pin gate this approach is not at all practical. In particular, when material in the gates freezes prematurely an adequate compensation for shrinkage can no longer be fully provided.

Finally, flow in the mold and the efficiency of mold packing diminish with increasing distance from the gate, and so large components often need to be fed through multiple gates

## I Mold cooling system

Mold cooling exerts a major influence on the overall cycle time, and therefore special attention should be given to its control. In addition however, it should also be as even as possible throughout the moulded component, and this requirement can often mean that several independent cooling circuits must be provided, so that different parts of the mold cavity can be cooled at different rates – in accordance with their needs.

As a general principle the use of many small channels with optimized cavity spacing is indicated in literature as being preferred over the use of fewer, larger channels with smaller spacing. However, detailed advice on the design and location of the mold temperature control system is best provided by specialists in this area.

The importance attached to the control of mould temperature, and its effect on the properties of the molded component is explained later

[See: *Conversion technology - Processing conditions – Mold temperature*], as is the effect of uneven cooling on shrinkage [See: *Conversion technology - Shrinkage*].

## I Vents

All cavities must be adequately vented so that air displaced by the incoming flow of raw material is properly evacuated. Insufficient venting can lead to burn-marks, bubbles, slow and incomplete cavity filling, and weak weld lines.

Vents should ideally be located as follows:

- In the last part of the cavity to be filled
- Where flow-fronts meet and form weld-lines.
- In the vicinity of features such as ribs that often have the potential for air entrapment.

## Component design

The design and shape of the component has important implications for machine selection and mould design. In addition however, it can also exert a major influence on fundamental requirements such as the mechanical performance of the component and its appearance.

A number of basic recommendations can be made, and a typical list is shown in Table 4, followed below by additional comments on most items.

Table 4: Some general principles applicable to component design

- | Allow an adequate draft angle or draw taper in order to facilitate smooth ejection (see additional comments below).

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- | Provide suitable tolerances to all dimensions, particularly in order to accommodate mould and after shrinkages (see additional comments below).

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- | Avoid abrupt changes in cross-section.

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- | Pay special attention to the design of any hinge sections (see additional comments below).

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- | Ensure that the gates and feeds to components incorporating a hinge are located in a suitable position relative to the hinge.

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- | Pay special attention to the design of any ribs and bosses (see additional comments below).

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- | Ensure that any undercuts are suitably designed and do not exceed established norms (see additional comments below).

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- | Avoid notches, and ensure that all changes in section are provided with an adequate radius (see additional comments below).

### | Draft/draw taper

It is generally accepted that a generous allowance is desirable, but most sources also agree that polypropylene will tolerate a smaller figure in certain circumstances. The allowance is usually quoted in the line of draw.

However, some moldings, for example certain paint containers are essentially straight-sided. The limit appears to be affected by the size and rigidity of those parts of the molding in contact with the ejector mechanism(s), and the resistance of the molding to buckling. In specific cases polish in the direction of draw can also help.

Finally, the cumulative affect of draw taper and component length should not be overlooked, and in particular its implication for dimensions. For example, a draw taper of 10 over a length of say 300 mm equates to a dimension change of over 5mm per side.

### | Dimensional tolerances

The overall dimensions and the tolerances specified on a component drawing should always be critically evaluated.

The spread of dimensions is in particular related to molding shrinkage, but in addition to items such as the accuracy with which the mold can be made, the accuracy and repeatability of the molding cycle, and to wear, etc. When quoting tolerances it should always be remembered that "tight" tolerances, that is minimal dimensional spread, are more difficult to achieve, and therefore invariably equate to higher costs.

### | Hinges

The excellent hinge-forming characteristics exhibited by polypropylene have lead to it being exploited in many different applications – in particular in hinged boxes and closures. The design and location of a hinge (i.e. the position relative to other parts of the molding, its thickness and its land-length) are extremely important. Among other things these factors exert a major influence on the transmission of pressure through the melted polymer, causing it to drop significantly as it passes through. This in turn retards the rate of polymer flow in the mold section beyond the hinge, and consequently it can affect mould filling in this section and the reproduction of mold detail.

The design and location of the gate(s) relative to the position of the hinge is another important factor. The subject of gates has been discussed previously [*See: Conversion equipment – Mould design*], but from the standpoint of optimum hinge performance the following additional conditions should also be fulfilled:

- The gate or gates should be located on only one side of the hinge – usually in the larger or major part of the mould.
- This larger part of the mold should ideally be completely filled before the melt reaches the restricted hinge area.
- The location of the gate or gates relative to the hinge should be such that the material flow is at right angles to the hinge line, and as even as possible.

The hinge section will be subjected to repeated stress during its service life, and so it is also important that the size of any molecular crystals should be kept to a minimum at this point. Large crystals can often lead to the development of micro-cracks when stressed, and in turn these can become initiation points for rupture failure. Consequently, the hinge should not be unnecessarily thick, and in any event this is a requirement reinforced by the fact that the hinge needs to exhibit easy bending through the angle of normal use.

## I Ribs and bosses

The main function of ribs is to increase the rigidity and strength of a molded article, without necessarily increasing its thickness throughout. In comparison, bosses are protruding studs which are generally used to align two or more component sections and to facilitate/secure a fit in their assembly. They are also used to accommodate fastenings or to increase strength in certain areas of the component.

Both must be carefully designed and located in order to minimise sink marks and stress concentrations. Many literature sources recommend items such as:

- The change in cross-section at the joint of the rib and the side-wall of the component should be equipped with a generous radius [*See: Notches*].
- The thickness of the rib should be no more than 50-70% of that of the side-wall.
- Ideally the height should be around 1.5 times the thickness.

In the event that these precautions are not taken then there is reported to be an increasing risk of unwanted witness marks.

Sometimes however, performance requirements necessitate the use of larger ribs, and a literature search suggests that on those occasions when this is unavoidable the resultant sink-marks can be disguised to a certain extent by:

- The introduction of a step in the critical section above the rib.
- The incorporation of a decorative bead over the rib.
- The provision of a textured surface.

Similar precautions to those outlined above for ribs are also relevant to the design of bosses. Some sources suggest that the risk of sink-marks can be minimized by coring part of the way into the thickness of the wall section to which the boss is attached. The usual recommendations for radii and draw taper also apply.

## I Undercuts

Many moldings incorporate undercuts, and in such cases it is common practice to accommodate the otherwise difficult ejection by the use of splits, side cores and plates typically actuated by angle-pins and so-called "dog-leg cams". However, this is not always the case, for example in components incorporating a snap-type closing feature, or in threaded components generally. In such instances the molding and its undercut must be "jumped" from the mold. It goes without saying that an ejection of this type should not be so violent as to cause damage to the molded component, and so an understanding of permissible boundaries is important.

Undercuts can be either internal or external – i.e. on either the inside or the outside of the molding. As a general rule they should be equipped with a suitably dimensioned lead-in angle, and the junction with the side-wall provided with a suitable radius. The efficiency of ejection is influenced by the type of polypropylene and its inherent flexibility, the rigidity of the component, by the moulding conditions selected, and by shrinkage.

The size of an undercut located on a circular part is usually calculated by expressing the difference between the maximum and the minimum dimensions as a percentage of the maximum.

The maximum permitted undercut is a matter of experience, and is best selected through consultation with a suitable mold-maker.

## I Notches

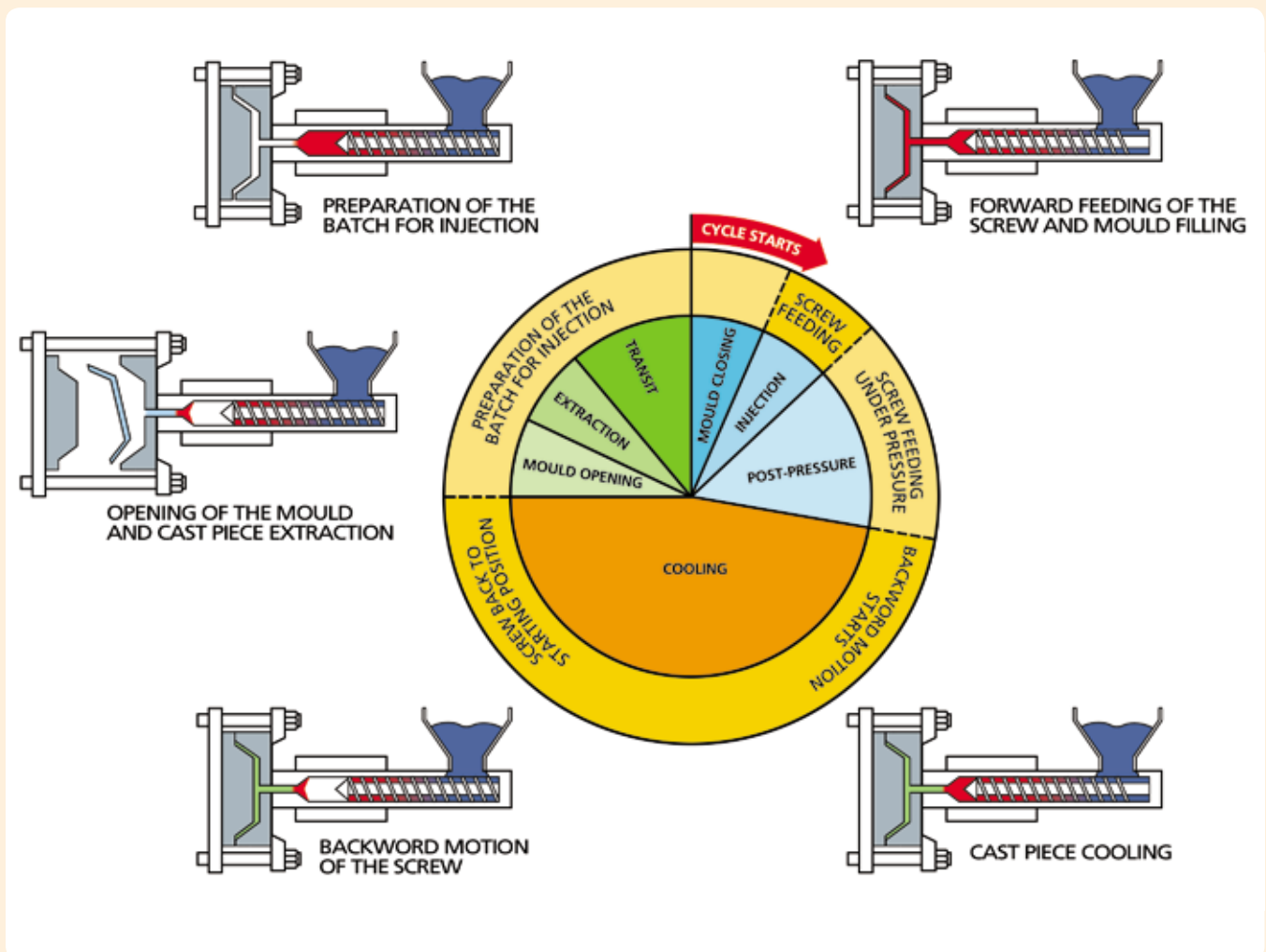
Like many other thermoplastic polymers, polypropylene resins are classified as being "notch sensitive", which means that in the presence of a sharp notch or an abrupt change in section they are prone to brittle impact failure where none would normally be expected. Consequently, changes in section and sharp corners should be provided with a suitable radius.

More information on notch sensitivity is provided at the end of this brochure, in the **Background note** on polymer characteristics.

# Conversion technology

The response of polypropylene to the conditions encountered during conversion into a finished component can often vary quite markedly from that of other raw materials. Furthermore, the very wide range of disparate components that are regularly molded from polypropylene inevitably require different molding conditions. It follows therefore that in addition to selecting the equipment commensurate with their requirements, and understanding the part played by the component design the potential converter should also have an adequate understanding of molding technology.

This part of the brochure provides advice on actual processing conditions, and this is followed by sections describing the molding performance of polypropylene and the complex subject of shrinkage.



## Processing conditions

The principle processing variables are melt temperature, mold temperature, injection pressure, after pressure, rate of injection and the plasticization conditions, each of which are discussed separately below. However, it should be clearly understood that these processing conditions are interactive, and that therefore a change to the set-value for one of them will have implications for the others.

For reasons of safety, great care should be taken when processing polypropylene at temperatures towards the high end of the above range – that is, at the temperatures typically associated with the production of thin-walled containers and other components requiring very high levels of flow. Polypropylene is extremely fluid at such temperatures

It is recommended that as far as possible molding is undertaken within the ranges established. However, it should also be clearly understood that while the advice provided is intended as a helpful guide, the precise settings will be influenced by a number of factors, some of which will inevitably be outside LyondellBasell's control.

**Therefore the potential converters should always satisfy themselves that their selected conditions are appropriate to their particular needs.**

### I Melt temperature

The melt temperature affects the ease of flow in the mold, the heat content and the melt volume. The selection and setting of the temperature will be influenced by the capacity of the injection machine, the configuration of the mold, the design of the component being produced and the characteristics of the polymer. As a general guide, and taking due account of the caveats mentioned above, when processing polypropylenes the heaters would usually be set so that the final temperature is within the range of ca 210 – ca 270°C. The temperature profile would normally be gradually increased along the barrel, from the hopper in the direction of the screw-tip. In addition, the temperature at the hopper-end of the barrel should be set at a level low enough to avoid premature melting of the pellets, even when there are extended pauses between shots.

As explained in the Background note on structure and properties, melt viscosity decreases with increasing temperature, and therefore the material flows more easily. In combination with other factors, viscosity and flow affect the degree of orientation, and consequently any change has implications for the level of shrinkage, internal stress and distortion. However, although orientation potentially increases with increasing flow, in practice the consequences are often masked because the effectiveness of after pressure (and its compensation of shrinkage) also tends to be enhanced at higher temperatures. The use of high temperatures usually also leads to enhanced replication of the cavity surfaces, and to improved surface gloss. At the extreme however, there is a danger of flash formation (typically at the parting lines, and in areas of wear/

damage to the shut-off faces), burn marks (at the vent ports) and even material degradation.

Conversely, the use of excessively low temperatures (with the attendant increase in viscosity and decrease in flow) can lead to short or incomplete components. Under certain circumstances excessively low temperatures can also lead to warpage and brittleness - particularly when the lack of flow has been offset by the use of increased injection pressure.

The use of low temperatures can also result in weak weld lines, because flow fronts may be too cold when they join together.

As the heat content increases with increasing temperature, plasticization becomes more efficient, and therefore the output from the injection unit generally increases. Mixing efficiency and homogeneity may also be enhanced, as may the impact resistance and the toughness. Conversely however, the increasingly hot polymer will inevitably take longer to cool down before it can be ejected, and so cycle times will probably have to be increased, and consequently overall outputs may fall. In addition, as explained later on slower cooling may also lead to changes to the crystal structure, and thereby to a possible increase in brittleness.

The melt volume increases with increasing temperature and then decreases again as it cools (i.e. the polypropylene first of all expands and then contracts). Whilst the polymer remains in a molten state compensation for this change can be made via the application of the after pressure. However, thermal contraction will continue after solidification, contributing to further shrinkage.

## I Mold temperature

The mold temperature directly affects the rate at which the polypropylene will cool-down and solidify, and therefore has an important bearing on the cooling time and on the overall cycle time. In addition, it also affects surface quality, mold shrinkage, and after-shrinkage. Mold surface temperatures of around 10 to 80°C are generally considered to be suitable.

The use of a high mold temperature leads to slower cooling, potentially longer cooling times and potentially enhanced surface quality. In addition, solidification occurs later-on, and so there is more time available for molecular orientation to dissipate. Consequently shrinkage may increase, and therefore it may in turn be necessary to apply the after pressure for an additional length of time in order to compensate for this effect. There is also more time for further crystallization to occur, and there tends to be further slight increases in both the density and the shrinkage. The actual size of the crystals also increases when the rate of cooling is slow - there being more time in which they can grow. Generally speaking toughness is often observed to decline with increasing crystal size, and brittleness to increase.

While the use of lower mold temperatures equates to shorter cooling times (and potentially higher outputs) there is an associated risk of solidification before molecular relaxation has had time to properly occur. This combination can sometimes lead to stress being "frozen-in" within the molding and thereby to shrinkage-related problems during service. Further information on this subject is provided later [See: *Molding performance – Shrinkage*], and also in the Background note on the structure and properties of polypropylene.

## I Injection pressure

The injection pressure must be set at a level sufficiently high to overcome the resistance encountered as the melt passes into the mould, otherwise short or incomplete components may result.

At the same time it should not be so high as to cause over filling, because this may result in flash-formation (typically at the mold parting lines), and even in the molded component becoming more difficult to eject. Furthermore, it may also lead to less obvious problems, such as brittleness and the possibility for post molding distortion, particularly if crystallization occurs while the melt is being highly stressed – a phenomenon known as shear induced crystallization [See: *Background note – Controlling parameters and the effects of change – Crystallinity and crystal structure*].

## I Injection speed

The speed of injection should be set at a level where without undue turbulence the cavities are filled sufficiently quickly to prevent premature cooling of the melt.

On the other hand, the rate should not be so fast as to lead to an undue degree of orientation, with the attendant risk of warpage and reduced biaxial impact resistance, or to cause air entrapment and subsequent burning.

As the polypropylene is forced through the injection unit and into the mold cavities it is subjected to shear forces, and the amount of shear developed increases with increasing injection speed. Polypropylene is particularly sensitive to changes in the level of shear in the melt, and this is a phenomenon that is fully exploited during the production of containers with thin or very thin side-walls [See: *Moulding performance – Flow in the mould*].



## I After pressure

The after pressure (also known as secondary or hold pressure) should ideally be applied for a time sufficiently long to fully compensate for the combined effects of thermal contraction, molecular relaxation and shrinkage. It is usually set at a level of around 50% of the injection pressure.

In practice however, it only remains effective while the gates are open. This is particularly relevant to those components in which the gate readily freezes (for example in the production of items with thin side-walls, fed by pin gates). On the other hand it is less of a problem in the production of larger moldings, where the gate remains open for longer, and where the after pressure can be applied for an optimum time period.

The use of excessively high pressures may once again lead to over filling of the mold. Conversely, lower after pressures may fail to fully compensate for the shrinkage.

## I Plasticization conditions

The plasticization conditions can affect the output from the injection unit, and the homogeneity of both the polymer and of the additives and pigments dispersed within the polymer.

Screw speed	Back Pressure
Mixing tends to become more efficient as the screw speed is reduced.	Mixing efficiency can be dramatically improved by the application of back pressure.
Ideally the speed should be set at a suitably low level, but not so low that plasticization no longer fits within the overall cycle without causing any hold-ups. In the extreme, the very high production rates at which components such as packaging containers with thin side-walls are usually produced mean that the converter has no alternative but to operate the screw at a relatively high speed.	The mixing efficiency is improved because the application of back pressure increases the level of shear developed by the screw. This is particularly important in the processing of blends and in the case of self-colouring by the converter. However its application also causes the melt temperature to increase, and screw-back to take longer.

## Molding performance

This part of the brochure explains what occurs to polypropylene during molding, and then describes in detail its response to the conditions encountered.

As always however with this type of document, some care needs to be exercised with the use of the information provided. The diversity of applications produced from polypropylene by injection molding is so great that such a document cannot cover every eventuality. Furthermore, the affects of changes to the principal material characteristics are not always easy to predict. Not only are they interactive with the molding performance, but other parameters (processing conditions, mold design and component design) also exert a significant influence, and are also interactive. In practice therefore the outcome from a change and its likely effect will depend on the overall aggregate, including both pros and cons.

### I Survey of the changes that occur during molding

By way of introduction this part of the brochure lists the principal changes that occur as the polypropylene passes through the injection machine and into the mold.

#### • Plasticization

As the granules leave the hopper and enter the screw they will start to melt under the influence of heat generated by the rotation of the screw (shear heat) and the heat coming from the heating elements on the barrel/cylinder.

The volume will change as the mixture of solid granules and air is compressed into an air-free melt. At the start of the sequence the density of the solid granules is ca 0.9 g/cm<sup>3</sup>, but the average density of the mixture of granules and air (known as the bulk density) is only around 0.6 g/cm<sup>3</sup>. However, as the screw rotates this mixture is compressed, and the air is forced-out backwards along the screw towards the hopper.

Under the influence of the increasing temperature the now essentially air-free mixture of molten and semi-molten granules will expand.

Under the influence of the increasing temperature the viscosity will fall, and fluidity increase.

Under the mixing action of the rotating screw the molten polymer will become homogenised, and at this point in the conversion process the density will have increased back-up to around 0.75 g/cm<sup>3</sup>. This is known as the melt density.

#### • Injection and mold filling

Under the influence of the injection pressure the melt will become very much more fluid – a phenomenon known as “shear thinning” [*See: Flow in the mould*].

Individual molecules within the melt will become oriented as they are forced through the runners and the gates.

The incoming melt will sweep air out from the formally empty mold through the vent ports.

The above molecular orientation will start to decay, as the oriented molecules attempt to return to their former configuration - resulting in shrinkage.

Additional material is forced into the mold to compensate for the above shrinkage.

#### • Mold cooling

The material within the mold starts to cool, through conduction from the sidewalls of the mold core and cavity, leading first of all to solidification at the surfaces.

As the gates freeze and the injection pressure becomes ineffective stress within the melt will start to dissipate, leading to shrinkage.

The component will also start to shrink as it cools, under the influence of thermal contraction.

There will be further contraction as the component solidifies throughout, and during this time the density will increase again – in the example given above, from the melt density of approximately 0.75 g/cm<sup>3</sup> back to the solid density of ca 0.9 g/cm<sup>3</sup>.

Crystallisation will occur



## I Melting and solidification

Being semi-crystalline in nature polypropylene resins have a precise melting point and an equally precise solidification/recrystallisation point.

The temperatures vary with the type of polypropylene – as shown in Table 5.

Clearly, the recrystallization temperatures are lower than the melting temperatures, and this characteristic, which is shared by many other semi-crystalline materials, is known as super cooling. In practice however its effects are readily accommodated during conversion.

A further characteristic of semi-crystalline polymers such as polypropylene is the absorption of an additional quantity of heat when they melt, and its subsequent release once again as they re-crystallize – known as the latent heats of melting and re-crystallisation respectively.

More detailed information and explanations on the subjects of melting and recrystallization are provided in the Background note on structure and properties at the rear of the brochure. The DSC tests described therein are undertaken under strictly standard conditions, because any variation in the latter has a direct affect on the result. Variations in conditions also influence the outcome in the molding machine and the mould, and while it is not possible to reproduce precisely the same level of control as in the testing laboratory, none the less effective control is important – particularly during cooling and solidification.

As explained when discussing the mold temperature (above), the rate at which the molten polypropylene is cooled has implications for both the level of crystallinity and the size of individual crystals.

Finally, a typical value for the thermal conductivity of polypropylene is 0.22 W/mK (at 20° C).

Table 5: Melting points and re-crystallization temperatures for a selection of *Moplen* polypropylene resins

Type of <i>Moplen</i> polypropylene	Melting temperature (°C)	Recrystallization temperature (°C)
Homopolymers and heterophasic copolymers	162-165	125-130
Random copolymers	142-146	110-120

## I Flow in the mold

Design considerations apart, basically speaking flow in the mold is controlled by the response of the polypropylene to the set conditions of both temperature and pressure/shear. In turn, this response is additionally influenced by the molecular mass of the polypropylene together with its molecular mass distribution, but these relationships are discussed in greater detail in the Background note on structure and properties [See: *Fundamental characteristics*].

On the one hand, the relationship with temperature is reasonably straight forward – melt viscosity decreases with increasing melt temperature, and therefore flow in the mold is enhanced. Conversely however, the relationship with pressure/shear is nowhere near as simple.

At very low levels of pressure/shear any increase has hardly any effect on the viscosity. However, as the pressure and shear are increased to the levels typically observed during injection moulding the viscosity reduces over-proportionately – the melt becomes ever more liquid and the throughput increases dramatically. As mentioned earlier, when providing an overview of the changes that occur during molding, this phenomenon is known as “shear-thinning” and it is one of the characteristics that make polypropylene so suited to injection

molding, and in particular to the production of rigid packaging containers with very thin side-walls.

Like certain other thermoplastic materials polypropylene resins are routinely characterized by reference to their melt flow rates – the latter being inversely related to the molecular mass, and more or less universally accepted as a “rough and ready” indicator of the same. However, this parameter is not entirely reliable as an indicator of likely flow in the mold. The level of shear at which it is determined is relatively low, and as such is in the area that is still largely insensitive to change. In comparison, the levels of shear encountered during molding are magnitudes higher, and tend to be very much in that area at which the rate of change of viscosity is at its greatest. Furthermore, and most significantly, different polypropylene resins can respond to changing shear in different ways – for example, those with a broad molecular mass distribution are more responsive than those with a narrower distribution. This important phenomenon is illustrated in Figure 2, which is a stylized representation of the response of two polypropylene resins, expressed in terms of changing viscosity with increasing shear stress.

Although the MFR is an imprecise indicator of likely flow in the mold, it still exerts an effect, and indeed the use of a polypropylene with an inappropriate

or “wrong” MFR can lead to serious problems. Flow increases with increasing melt flow rate, and vice versa. As with the melt temperature, when the melt flow rate is too low there is a danger of short or incomplete moldings. In addition, under certain circumstances there is also a danger of distortion resulting from high levels of internal stress when the lack of flow has been offset by the use of excessive pressure. Alternatively, when the melt flow rate is too high there is a danger of the formation of flash, and possibly burning at the vent ports.

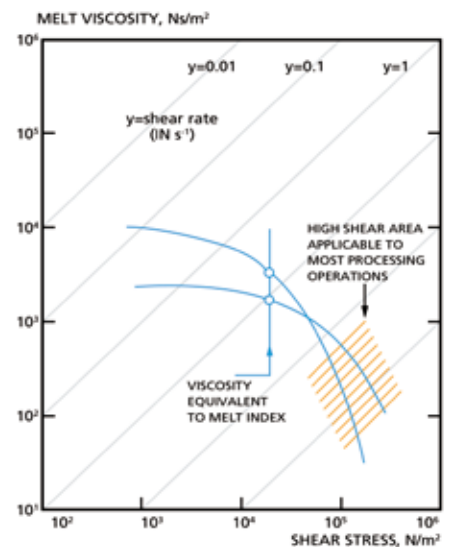
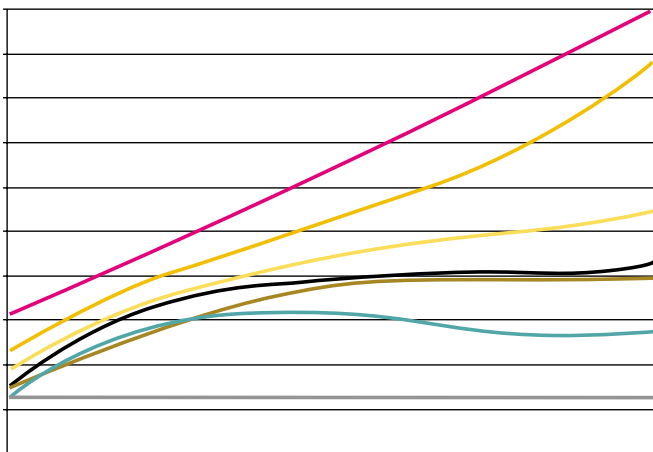


Figure 2: Example of poor prediction of flow at high shear conditions via melt index measurements



## I Coefficient of linear thermal expansion

Knowledge of expansion characteristics is important when selecting materials and designing components that will be used at elevated temperatures.

The variation of linear thermal expansion coefficient ( $\alpha$ ) with changing temperature is shown in Figure 3.

Figure 3: Typical linear thermal expansion coefficient ( $\alpha$ ) of different polypropylene resins measured in the direction of flow, in comparison with aluminium.

## Shrinkage

Shrinkage is influenced by almost all of the major parameters discussed in this brochure – namely, the properties of the polypropylene, the processing conditions, the design of the mold and the design of the component. It is the product of thermal contraction as the component cools in the mold cavity, decompression following the removal of the injection pressure, relaxation as molecules disturbed under shear attempt to return to their natural state, and crystallization as molecular chains adjacent to each other become more closely packed.

A proper understanding of shrinkage behavior is essential to the setting of dimensional tolerances. However, as may be seen from the above description, it is a complex subject. Furthermore, it does not necessarily occur in a conveniently linear fashion – for example, some parts of the component may shrink differently to other parts, thereby leading to warpage and distortion, and moreover further low-level shrinkage can also occur with time after moulding.

### I Mold shrinkage

Most shrinkage occurs in the mold, and during the first few hours after ejection, and for the purposes of this brochure this is what is meant by the term “mold shrinkage”. By way of introduction the shrinkage exhibited by polypropylene resins can typically vary between 1 and 3%, dependant on the properties of the polymer, the processing conditions, the mould design and the component design. The importance of these parameters to the control of shrinkage cannot be overstated, and so the most careful attention therefore needs to be given to them.

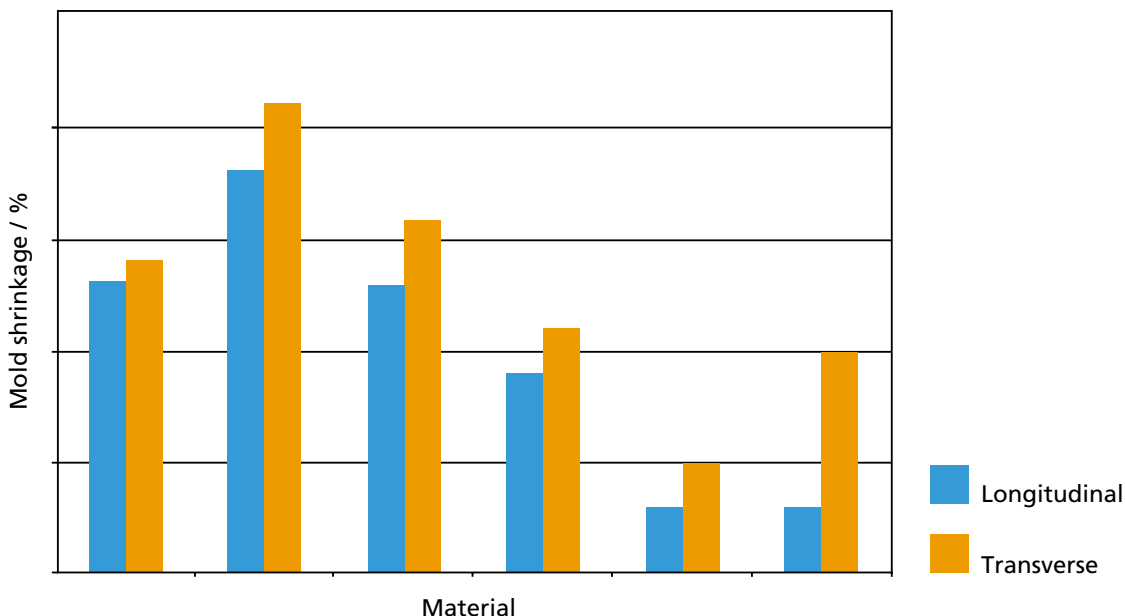
For guidance, a testing of mold shrinkage may be conveniently undertaken by the molding of film-gated plaques under standardized processing conditions, and then measuring their dimensions, both in the direction of flow and at right angles, for the first few hours after ejection. Specimen results are shown in Figure 4. (NB the values quoted are for guidance only, and do not obviate the need for appropriate tests).

As explained when discussing the design and location of the gates, it is crucially important to maintain flow in the mold for as long as possible during the application of the after pressure.

Optimum control of shrinkage can no longer be fully realised when the material in the gates freezes prematurely. When this happens flow in the mould ceases, and so further shrinkage cannot be compensated.

Finally the efficiency of mold packing diminishes with increasing distance from the gate, and so shrinkage tends to increase in these areas.

Figure 4: Typical shrinkage behaviour for selected polypropylenes



## I Differential shrinkage, distortion and warpage

Warpage and distortion are caused by the release of localized areas of stress, which in turn are often the result of uneven shrinkage in various parts of the component. However, the factors affecting these unwanted phenomena are reasonably well understood, and so they can usually be controlled within acceptable limits by the application of a series of basic ground-rules.

Once again, it is important to ensure that the rate of cooling is as even as possible throughout all parts of the component. One of the commonest causes of distortion is the presence of both thick and thin sections, side by side within the same component – for example, load-bearing ribs/columns in a crate. Thick sections cool more slowly than thin ones, and therefore exhibit greater shrinkage. Consequently, the presence of thick and thin sections within the same component will clearly lead to a potential for imbalance, and so in order to restore equilibrium the heavier parts will require more effective cooling. In practice this is often achieved by the use of separate cooling channels that can be independently controlled.

Even components of uniform thickness can also suffer a potential cooling imbalance, because the material closest to the gates will tend to be warmer than that at the periphery. Once again, cooling should be preferentially directed to the warmest part, using the same principles as detailed above.

Distortion can also be caused by excessive differences between shrinkage in the line of flow and that in the transverse direction. The amount of shrinkage obtained is largely influenced by the degree of molecular orientation caused during moulding, and by the efficiency of after pressure relief. As mentioned earlier [**See: Flow in the mould**] increased levels of orientation are encountered at high levels of shear. For example, the use of

with increased injection pressure can cause excessive orientation, leading in turn to warpage and brittleness.

Differential shrinkage is also influenced by the width of the molecular mass distribution, with polypropylenes having a relatively narrow distribution (for example, controlled rheology *Moplen* grades and *Metocene* polypropylene resins) exhibiting generally more balanced shrinkage. Finally, the enhanced ease and speed of mould filling exhibited by high flow polypropylenes means that there is relatively more time available for the dissipation of internal stress, and more time available for the compensatory application of the after pressure. Consequently in practice such high flow grades also tend to exhibit less shrinkage.

## I Sinks and voids

Sink marks and voids are a further manifestation uneven shrinkage. They are commonly related to the design of the component, and can sometimes be rather difficult to eliminate.

Sink marks are slight depressions visible on the surface of a molded component. They are a local phenomenon and occur when shrinkage cannot be properly compensated by mold packing. They tend to be observed either at the end of a flow-path, typically on the rim of a component, or at points where thick sections are fed by surrounding thin ones, such as where a rib or a boss meets a side-wall. Provided that the component or mold designs are not limiting factors, they may be reduced by improving the effectiveness of the after pressure, or by using a polypropylene that flows more easily. In addition, their appearance can sometimes be disguised to a degree by changes to the surface finish in the effected areas.

Voids are actual cavitations within the structure of the component. They are similar to sink marks in so far as they are caused by inadequate mould packing in a localised area. However, in this case the surface of the molding will have solidified, often very rapidly, while the center is still molten. The latter then continues to shrink, and so in order to relieve the developing stress imbalance a cavity develops.

## I After shrinkage

After shrinkage is a term coined to describe the continuing change in dimensions that sometimes happen well after ejection from the mold, and during service life. It usually occurs at a relatively low level, and is typically the result of further slight molecular contractions associated with continuing recrystallization.

Sometimes however, increased levels are observed, in particular under the influence of high service temperatures. Such shrinkage is principally caused by the post moulding dissipation of internal stress. It is frequently localized, within one or more parts of the molding, and can often lead to warpage.



## Trouble-shooting

A comprehensive trouble-shooting guide, featuring common molding faults together with their suggested remedies, is available in a separate LyondellBasell brochure, entitled **“Polyolefins - Injection molding trouble-shooting”**. Copies may be obtained from local sales offices and technical centers, and online at [www.polymers.lyondellbasell.com](http://www.polymers.lyondellbasell.com).

# Ecology and life

LyondellBasell is very conscious of its environmental responsibilities and is continually developing technologies which can improve the environmental performance of both our operations and our products.

The advantages arising from improvements in our conversion technology, coupled with the availability of more sophisticated polypropylene, have been discussed at various points in this brochure. Historically, these technology improvements have also generated improvements in environmental outcomes, as equivalent performance has often been maintained whilst reducing the consumption of raw materials and energy. The production of polypropylene can be described as being a high conversion- high yield process, as a very low proportion of raw materials leave the process as either waste or emissions.

Despite these advances, energy use remains an area of focus for LyondellBasell, as both polymer production and molding are energy intensive processes. Whilst LyondellBasell

continues to develop products that converters can process with a lower energy requirement and less polymer use, the polymer conversion process is generally more energy intensive than polymer production, per unit weight. Therefore, it is important for converters to minimize their energy losses during each stage of the conversion process. The design and section of equipment, and the process layout are extremely important for minimizing energy losses due to the excessive use of heating, cooling or equipment pressure. Additional guidance material be obtained via documents such as the European Best Practice Guide: Low Energy Plastics Processing, 2006, or via your Sales Representative.

Finally, it is noteworthy that as Environmental pressures continue to drive the selection of end-use applications

with a favourable environmental profile, that polypropylene is often a material of choice. Continual improvements in the technical properties of polypropylene have enabled them to become lighter and stronger in comparison to other materials, and therefore polypropylene is often used in applications where energy, fuel or water conservation is important. Applications such as packaging or automotive continue to reap benefits such reduced food wastage due to improved packaging, and fuel consumption savings in vehicles.

Table 6 shows the life cycle benefits arising from the use of polypropylene, and is intended to illustrate the advantages of this type of material over many of the alternatives.

- | Relatively low energy consumption during resin production and conversion in comparison to the energy savings that can be realised during the lifetime of the final product application.
- | Production processes generate low water and air emissions.
- | Highly efficient utilization of raw materials minimizes solid waste during polymer production and conversion.
- | Inherently low weight and product packing efficiency minimizes transportation requirements and fuel usage
- | Polyolefins are suitable for recycling or energy recovery, enabling waste to be diverted from landfill.
- | Polypropylene has a high calorific value, and can contribute greatly to energy recovery

Table 6: Life cycle benefits of polypropylene resins during manufacture, use and recovery

# Material form and availability

## Pre-drying and storage

LyondellBasell's European materials are usually sold as natural, un-coloured pellets, supplied in 25 kg sacks or silo trucks (about 25 tonnes).

The original packaging of the polypropylene provides a level of protection against the ingress of moisture and dirt. Pre-drying is usually not necessary, but under certain climatic conditions such as large temperature differences coupled with high atmospheric humidity, moisture may condense inside the packaging. It is therefore recommended that in accordance with good practice, warehouse and storage areas be adequately ventilated. In addition, experience shows that it should also be sufficient to place the material into the same climatic conditions as the molding machine prior to conversion.

Exposure to UV radiation and to high temperatures during storage can damage the product. It should therefore be protected from direct sunlight and temperatures above 40° C.

## Compatibility and miscibility

All *Moplen*, *Adstif*, *Clyrell*, *Metocene* and *Purell* pelletized resins are in principle compatible and miscible with one another and with other polypropylene grades of the same general type.

However, due to the relatively limited homogenization capacity of many injection molding machines it is recommended that unduly large differences between the melt viscosities of blend components should be avoided. Blends of polypropylene with other thermoplastic materials should also be avoided.

## Pigmentation

On those occasions when colored packaging is required the pigmentation will usually involve the use of a masterbatch.

It is essential that all components of the masterbatch should comply fully with the requisite regulations, and particularly those covering use in contact with food. In addition, it is recommended that the pigment carrier is either based on a polypropylene, or that it should be fully compatible with the material being colored. In addition, all pigments should be sufficiently heat stable.

## Recycling

In certain cases production scrap such as sprues and reject moldings may be recycled in the form of a blend with the virgin polypropylene. However, the use of such material is dependant upon the conversion process and the final application, and on any specific performance requirements.

Such material needs to be re-granulated so that it may be blended back with the virgin granules. It is important that the viscosities of the virgin and the scrap materials do not differ excessively, and that the regrind material is clean and has not been thermally degraded. Furthermore, the regulatory bodies in Europe have introduced severe restrictions on the use of regrind material in direct contact with food.

# Background Notes – Structure and properties of polypropylene

The characteristics and properties of the polypropylene resins are of fundamental importance to both a smooth and effective molding operation, and a successful performance during the service life of the component. In order to help those customers who may be relatively unfamiliar with this subject, this background note provides some explanations of the basic terminology often used to describe polypropylene, and then goes on to describe its production and its principle physical properties.

## Definitions and terminology

The properties of the polypropylenes are influenced by a number of parameters, one of the most important of which is their basic form and molecular structure.

Polypropylene resins are defined as being semi-crystalline. As explained later, some of the molecular chains are able to pack relatively closely together, and this leads to the formation of a limited amount of highly ordered crystalline areas. In comparison, the molecular structures of certain of the other polymers commonly converted by injection molding are much less ordered, and as a consequence they tend not to form crystalline areas. This group of polymers are defined as being amorphous. A diagrammatic representation of these two basic structures is shown in Figure 5.

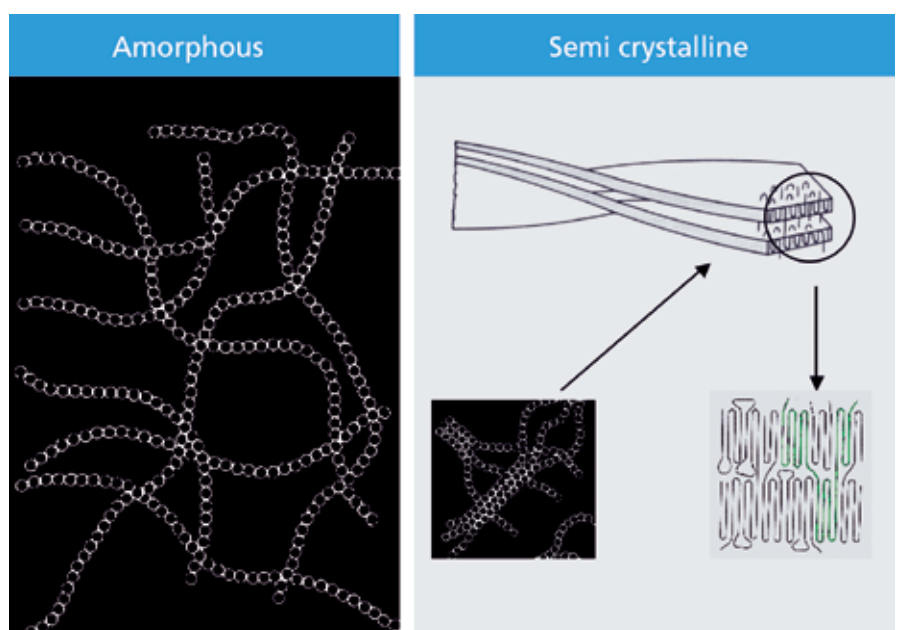


Figure 5: Basic structures of common thermoplastics



As explained earlier [See: *Conversion technology – Moulding performance – Melting and solidification*], semi-crystalline polymers such as polypropylene exhibit a clearly defined melting-point, or  $T_m$ , and an equally clearly defined re-crystallization temperature or set-up point, known as  $T_x$  or  $T_c$ . The precise values vary with individual types and individual grades. For example, the melting-point of a general-purpose *Moplen* homopolymer is in the region of 162 to 165°C, whereas that for certain *Moplen* random copolymers are in the region of 142 to 146°C. In comparison, amorphous polymers exhibit neither a melting point nor a set-up point, but merely become softer as the temperature is increased and then harder again as the temperature is reduced.

To a certain extent, the properties exhibited by polypropylene resins are related to their glass transition temperatures, or  $T_g$ s. The latter are classically defined as the temperatures below which molecular motion largely ceases. This has important implications for the absorption of energy, and at temperatures below the  $T_g$ , where there is only a minimal amount of molecular motion, polymers tend to behave in a glassy fashion. A typical  $T_g$  for *Moplen* homopolymer would be in the region of 0°C, and that for *Moplen* heterophasic copolymers typically depressed down to -55°C. In general terms therefore, at chill temperatures homopolymers whilst still relatively strong are becoming somewhat borderline for the onset of brittleness, whereas heterophasic copolymers are exceptionally tough. On the other hand the homopolymers are rather rigid whereas the copolymers more flexible.

Needless to say, there are inevitably exceptions to such generalizations, and in particular the numerous grade variants that are available from LyondellBasell have in part been developed to overcome many generic deficiencies in performance, and to enhance certain key properties.

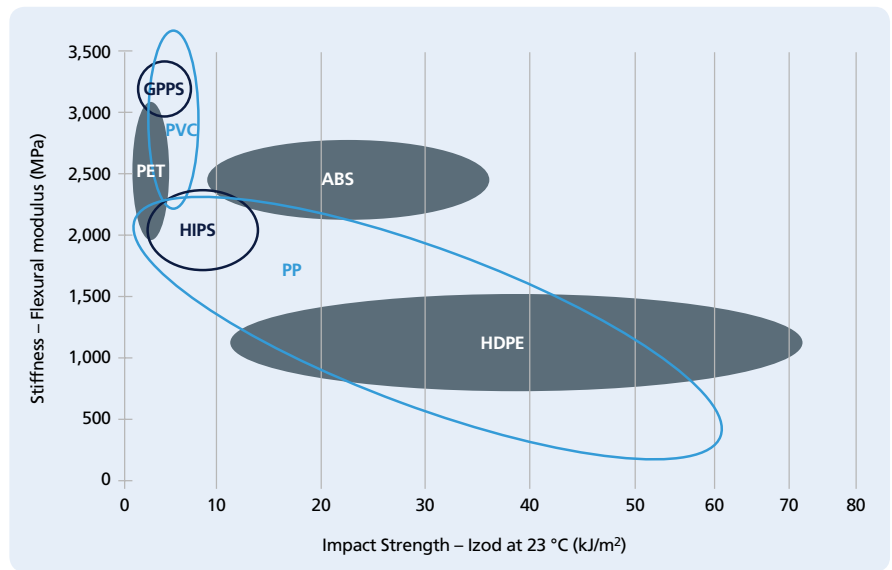


Figure 6: Polypropylene and other common thermoplastics – Stiffness Vs impact strength

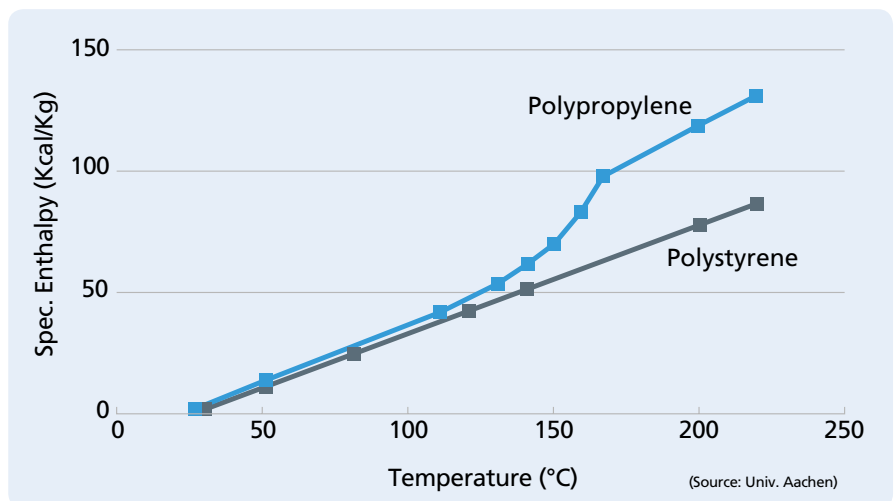


Figure 7: Comparative enthalpy curves – Polypropylene and polystyrene

In order to facilitate an overall comparison, the rigidities and the abuse resistances of polypropylene resins generally are presented in Figure 6, together with those for other common thermoplastics. Stiffness is measured as flexural modulus, and abuse resistance as Izod impact strength.

When semi-crystalline polymers such as polypropylene melt they absorb an additional quantity of heat – known as

the latent heat of melting. Furthermore, this heat is “given back” during solidification – known as the latent heat of re-crystallization. In comparison, amorphous materials such as polystyrene do not exhibit these phenomena – in so far as they are non-crystalline. This difference may be conveniently expressed by reference to comparative enthalpy curves, two of which are presented in Figure 7.

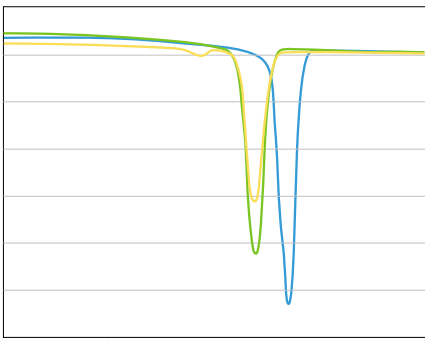
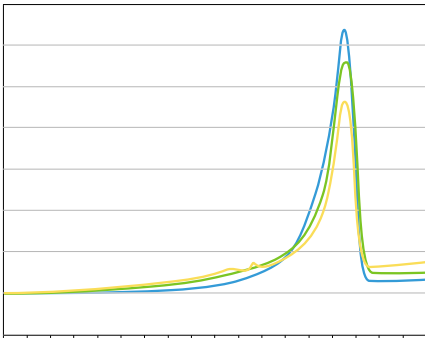


Figure 8: Typical DSC curves for a homopolymer polypropylene

Arguably of even greater significance, these quanta of heat or latent heats form the basis of an exceptionally important laboratory test to accurately determine the melting and re-crystallisation temperatures – known as **DSC** (differential scanning calorimetry).

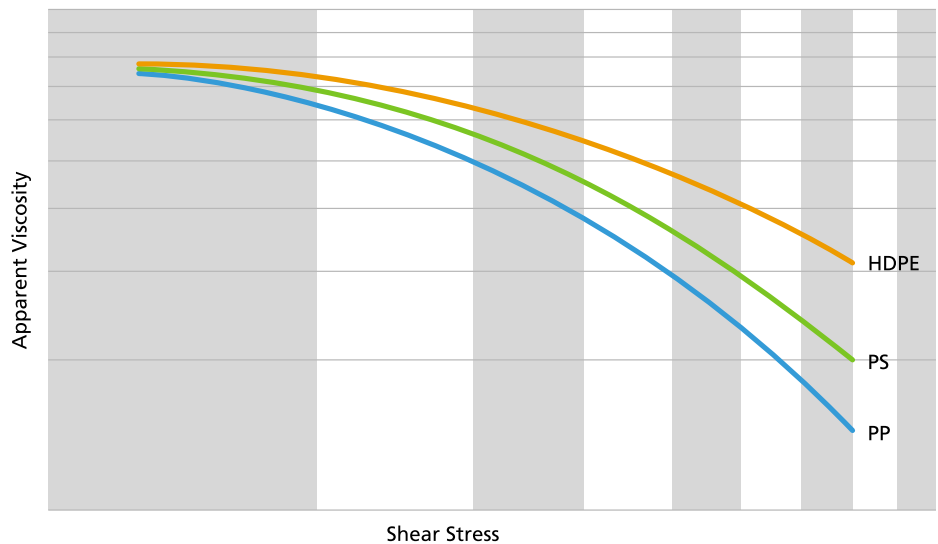
In order to eliminate any possible side-effects and to enhance reproducibility the test conditions must be rigorously controlled, but as shown in Figure 8, the results are exceptionally precise.

When the subject of flow in the mold was discussed earlier in the brochure it was explained that from a molding stand point the major determinants are the level of pressure/shear applied and the temperature selected. At very low levels of pressure and shear any increase has hardly any effect on the fluidity (known as its **melt viscosity**). However, as the pressure and shear rate/stress are increased to the levels typically observed

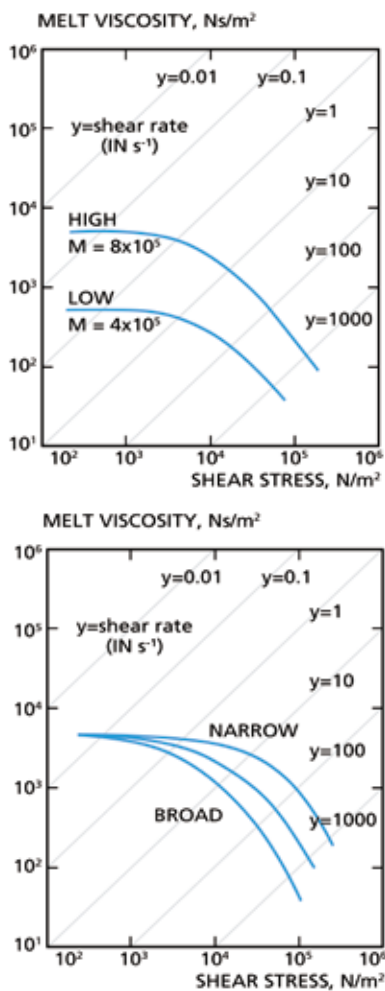
during injection molding the melt viscosity reduces over-proportionately – the melt becomes ever more liquid and the throughput increases dramatically. The melt is described as being either **thixotropic** or **pseudoplastic**, and the phenomenon is referred to as **shear-thinning**.

A representation of the relationship between changing pressure/shear and viscosity for polypropylene in comparison with other selected materials is shown in Figure 9.

Figure 9: Typical relationship between apparent viscosity and shear stress for selected raw materials.



As may be seen from the above curve, polypropylene is particularly sensitive to changing shear (known as **shear sensitivity**), and as explained earlier it is this characteristic that makes it so suitable for injection molding, and in particular for the production of thin-walled components.



When discussing flow in the mold it was also explained that the response of the polypropylene to changes in pressure and temperature were in turn influenced by the following material parameters, namely:

- **Molecular mass**
- **Molecular mass distribution**

In essence, the melt viscosity increases with decreasing molecular mass, and with increasing width of distribution. Typical curves illustrating these effects are presented in Figure 10.

In structural terms polypropylene resins are organic in nature, and are based on a very large number of repeated units containing carbon and hydrogen. Many such materials, and including the polypropylene resins, require the addition of **thermal stabilizers** to limit molecular breakdown during exposure to heat and shear.

Figure 10: Typical shear stress/viscosity curves showing the effect of changing  
a) Molecular mass  
b) Molecular mass distribution  
(NB the cross-hatchings refer to the shear rates).

The **organoleptic** properties mentioned earlier are those associated with taste, odor and smell. They are controlled partly by the inherent characteristics of the polypropylene and partly by the characteristics of additives included in the formulation, and then crucially by the reaction of these factors to the forces of heat and shear encountered during conversion. Further details are provided later-on [See: *Other important properties – Organoleptic characteristics*].

## Fundamental characteristics

Polypropylene resins consist of long polymer chains made up of repeating units of the monomer unit, propylene. The structure of the latter is more complex than that of the ethylene used for the production of polyethylene. In particular, in each monomer unit one of the hydrogen atoms has been replaced by a so-called methyl group (CH<sub>3</sub>), giving the following structure.

During polymerization not only do the monomer units join together, but under the influence of the catalysts used in the production process (known as **stereo-specific catalysts**), each of the incoming monomer units is marshalled in a controlled manner. This control is extremely important, and has major implications for the structure and properties of the polypropylene.

In the case of a less complex polyolefin made by such a catalyzed process (for example, high density polyethylene), the position of any one in-coming monomer unit relative to the growing polymer chain is not particularly relevant, in so far as

each molecule of monomer (ethylene) is symmetrical. However, propylene is not symmetrical, and it is the configuration of the methyl side-groups relative to each other once the monomer units are all joined together in a polymer chain that is so important.

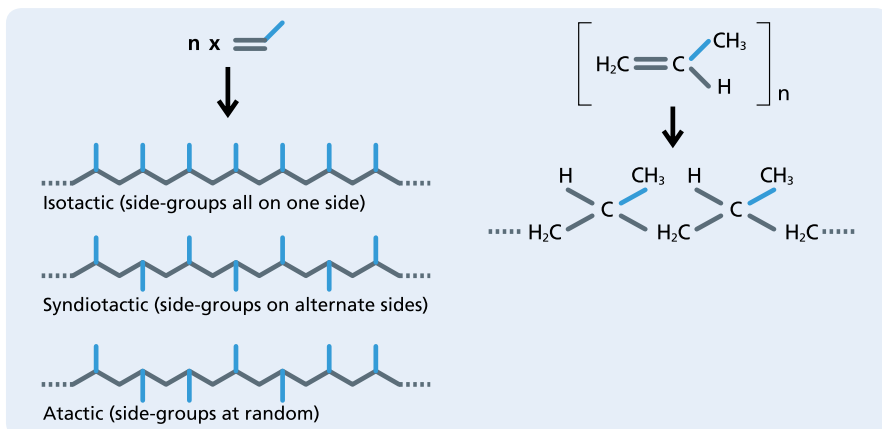


Figure 11: Diagrammatic representation of the fundamental structures of polypropylene

The basic structure of polypropylene is shown in Figure 11. Three configurations are theoretically possible. One in which the side groups are all on the same side of the polymer chain or backbone (known as **isotactic**), one in which they are on alternate sides (known as **syndiotactic**), and one in which they are distributed at random (known as **atactic**). Commercial grades usually contain around 97 % of the isotactic variant, together with 3 % of atactic, and virtually none of the syndiotactic variant. These figures can be varied somewhat by altering certain process parameters during the manufacture of the polypropylene, or alternatively by changing the catalyst. However, since each configuration tends to exhibit its

own balance of characteristic properties the ratio to each other is important. With the exception of highly specialized materials, the above ratio is generally recognized as being typical for most of the grades available today.

Polypropylene has previously been classified as "semi-crystalline". Generally speaking it contains between 50 and 55% of crystalline material. The remainder is a mixture of partially crystalline material, known as **smectic**, and amorphous material. Crystallization occurs when adjacent chains and parts of chains are lying sufficiently close to each other. However, on a molecular basis the methyl side-groups are relatively large, to the extent that the

group from one unit would spatially interfere with the one from the adjacent unit. Consequently, as the chains pack together and crystallization occurs the side-groups become displaced radially around the backbone – a phenomenon known as **steric-hindrance**. The result is a helical structure, in which three monomer units are involved in one complete 360° turn. A pictorial representation of this spiral is shown in Figure 12.

The net result of these various factors is the formation of a rod-like molecular structure, and this in turn is the reason why homopolymer polypropylene resins are a relatively rigid example of a semi-crystalline polymer.



Figure 12: The spiral structure of polypropylene

## Manufacture

A major part of LyondellBasell's production of polypropylene is based on the use of modern derivatives of catalysts originally developed by Professor Natta on behalf of their heritage company, Montecatini. More recently LyondellBasell has also introduced an alternative technology, based on the use of metallocene catalysts.

Professor Natta was one of the pioneers of the polymerization of propylene into polypropylene. He applied the general principles developed previously by Professor Ziegler. Many sources (but not all) attribute the original development of this type of catalyst to his research work, and so consequently the catalysts carry their joint names. These catalysts are now universally established for the manufacture of polypropylene, and products based on their use have been shown to exhibit an excellent combination of physical properties in the market for injection molding.

The world's first manufacturing facility was established in Ferrara, Italy in 1957, using the newly-discovered catalysts. Understandably, by modern standards the products were relatively unsophisticated, and in addition required a considerable number of finishing stages before they could be released to the market. However, over the years many new and improved generations of Z-N catalysts have been developed, leading to the gradual elimination of the majority of the former finishing steps.

Concurrent with these improvements to the efficiency of the catalysts, Himont also concentrated on the development of manufacturing technology and hardware, and this led to the successful introduction of the *Spheripol* process in 1982 – a picture of which is shown in Figure 13. Through their licensing activities this has become the most widely-used manufacturing process in the entire world, and is routinely employed for the manufacture of homopolymers, heterophasic copolymers and random copolymers.

In the early days of the process and catalyst developments polymerization

was undertaken in a single reactor, using what is known as the **slurry** process. Propylene monomer gas was bubbled through a fine dispersion of catalyst suspended in a liquid diluent – usually a suitable alkane. As time went by additional reactors were added, either to enhance control, or to facilitate the production of heterophasic copolymers, and in due course the use of an alkane diluent was replaced by liquid propylene. In addition, alternatives to the slurry process, known as **gas-phase** or **bulk** techniques were also introduced.

However, the next major advance in polypropylene manufacturing technology came with Basell's introduction in 2002 of its revolutionary *Spherizone* process. This process is undertaken in a single reactor containing two different environments with two distinct fluid dynamics regimes. As the polymer granules form they circulate continuously from one zone to the other. The two zones are separated by an injection of barrier liquid, enabling different gas compositions to be maintained in each environment. This allows the formation of uniform, highly homogeneous polymers with significantly expanded property profiles and types.

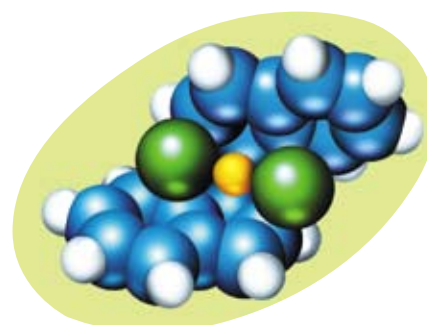
LyondellBasell's involvement with the development of an alternative catalysis system, based on the use of metallocene complexes was briefly mentioned above. Throughout the 1980s, and building on the work undertaken with polyethylene, other LyondellBasell heritage companies (Hoechst and BASF) gradually applied the science of these single-site catalysts to the production of polypropylene. The materials produced were still generically polypropylene resins, but they exhibited a subtly and interestingly different balance of properties. A drawing of a metallocene molecule is shown in Figure 14.

LyondellBasell's metallocene-based polypropylene is sold under the trade name *Metocene*, and they have now been commercially available for a number of years. More detailed information comparing the properties of *Metocene* and Z-N polymers are provided later [*See: Types of catalysts used during polymerization*].



Figure 13: The characteristic *Spheripol* double loop.

Figure 14: The metallocene molecule



## Controlling parameters and the effects of change

The properties of polypropylene, as expressed both in its response to the conditions encountered during injection molding, and in the physical properties of the finished components are largely controlled by a number of basic parameters.

- Basic types of polypropylene
- Crystallinity and crystal structure
- Molecular mass and melt flow rate
- Molecular mass distribution
- Presence of selected additives.
- Types of catalyst used during polymerization

### Basic types of polypropylene

As mentioned at various points in the brochure, three basic types are routinely available - homopolymers and two types of copolymers.

A comparison of selected properties is presented in Table 7, from which it can

be seen that homopolymers have the best rigidity, random copolymers have the best transparency and heterophasic copolymers have the best impact resistance.

Table 7: Comparison of the material properties of the basic types

	Rigidity	Abuse Resistance	Transparency
Homopolymers	1	3	2
Random copolymers	3	2	1
Heterophasic copolymers	2	1	3

1 - Highest 2 - Intermediate 3 - Lowest

The molecular chains in homopolymers are derived solely from the polymerization of propylene monomer units. The resultant polymers are more flexible than amorphous materials such as crystal polystyrene or PVC, but as a consequence of their rod-like structures [See: *Fundamental characteristics*], this difference is not as large as it otherwise might have been. The glass transition temperatures of LyondellBasell's *Moplen* homopolymers typically lie in the region of 0 and 5°C, and their

resistance to impact abuse declines at temperatures below this range.

The structure of the random copolymers and the heterophasic copolymers (latter also known as block or impact copolymers) are more complex. Both contain a second monomer (usually ethylene), but the configuration of the monomer units within each one is different, as shown in Figure 15. Each has its own, individual molecular structure, and each exhibits specific physical properties and offers the end-user a particular balance of performance.

Figure 15: Types of copolymer

#### Random Copolymers

Single phase polymer: chain consists of polypropylene units and randomly distributed comonomer units



#### Heterophasic Copolymers

Multi-phase copolymer: polypropylene homopolymer and ethylene-propylene rubber

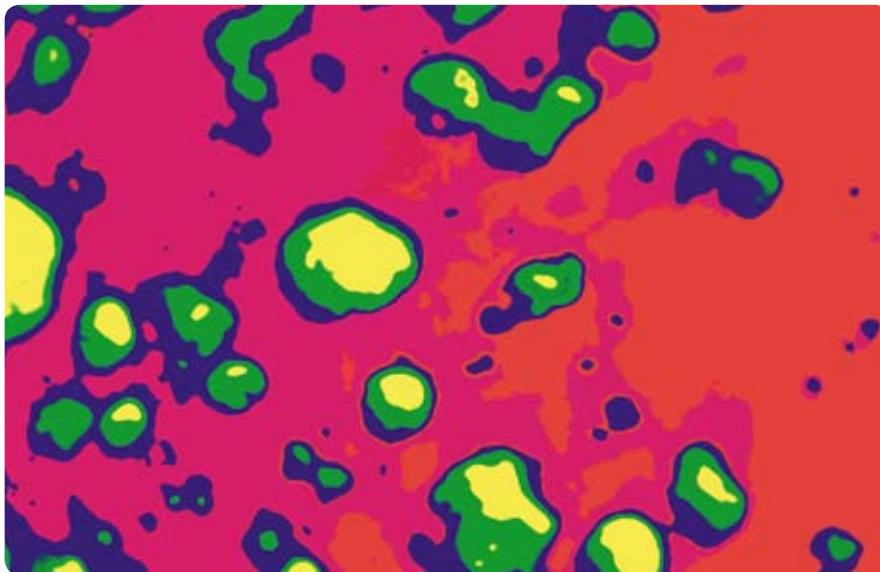


The second monomer used in the production of random copolymers is distributed without any particular order amongst the propylene units - all on the same chain. Consequently, like homopolymers they can be designated as being **single phase** materials. The amount of co-monomer present in a random copolymer typically varies between 1 and 5%. LyondellBasell's *Moplen* random copolymers are characterized by a high level of transparency, excellent gloss, and improved resistance to impact abuse (compared to homopolymers).

The heterophasic copolymers are produced from a reactor blend of a homopolymer and a separate rubber - most often an ethylene-propylene rubber. Generally speaking, they are characterized by excellent resistance to impact abuse (particularly at low temperatures), a reasonable level of stiffness, but opacity rather than transparency.

The amount of rubber will vary with the grade, and with the balance of physical properties required. The resistance to abuse exhibited by these copolymers improves with increasing rubber content. At the same time the glass transition temperature is markedly depressed, thereby making them increasingly suitable for use at low temperatures. A photomicrograph of dispersed rubber particles is shown in Figure 16.

Figure 16: TEM (transmission electron microscope) photomicrograph showing rubber dispersion.



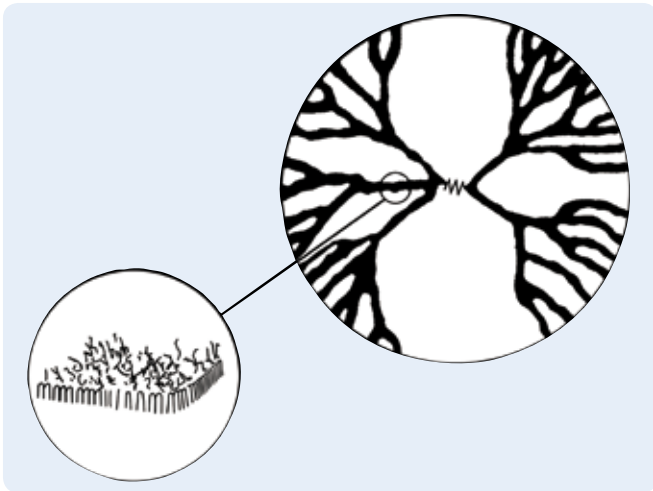


Figure 17: Diagram showing growth pattern of structural features from a nucleus.

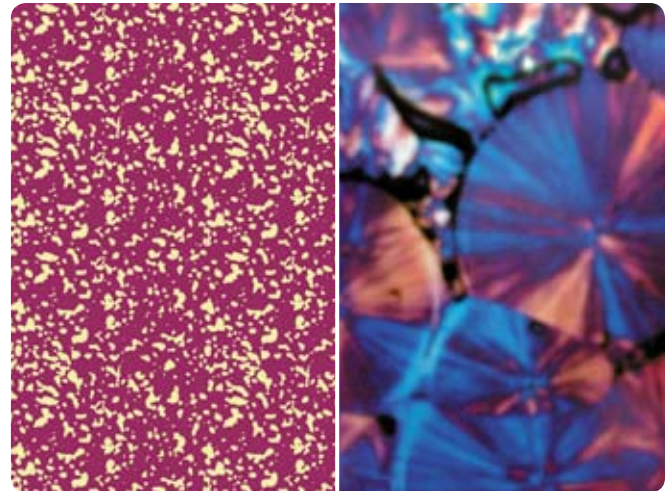


Figure 18: Crystal structure of rapidly cooled polypropylene (left) and slow cooled polypropylene (right).

## I Crystallinity and crystal structure

Generally speaking the 50 – 55% crystalline material typically observed in regular polypropylene is mid-way between those in low density and high density polyethylene. However, this is not the complete story, in so far as the size and shape of individual crystals is influenced by the thermal history to which the polypropylene has been subjected during molding, and the presence/absence of a nucleating agent. In addition, LyondellBasell has for some years been able to produce special polypropylene resins exhibiting a higher level of crystallinity.

Crystals of polypropylene are generally thought to grow in **fibril-like** structures from a central point or nucleus – as shown diagrammatically in Figure 17.

When polypropylene is subjected to rapid cooling, particularly in thin sections, a multitude of crystals start to grow, all at the same time. This very high rate of initiation leads to the limited amount of crystallisable material being used-up rather quickly, and consequently the individual crystals remain only small in size. As explained below, a similar effect is seen in the presence of a nucleant.

In comparison, when molten polypropylene is subjected to slow cooling the rate of initiation is significantly reduced, and although the amount a crystallizable material is roughly the same as before, each crystal now has less competition from its neighbors. Consequently, the crystals are larger, as shown in Figure 18.

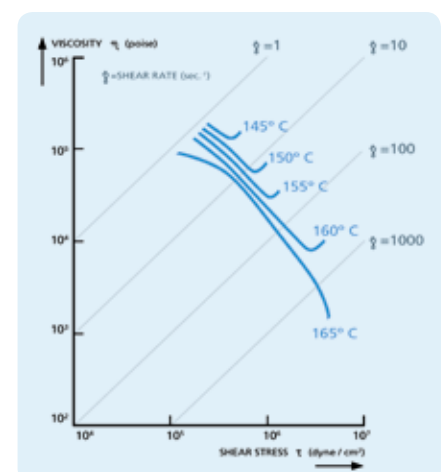
The crystal structure resulting from slow cooling, although visually attractive when viewed through polarised light, can however be associated with brittleness. This is related to a tendency for the formation of micro-cracks around their boundaries when subjected to stress.

Earlier in the brochure mention was made of a phenomenon known as shear-induced crystallization or SIC [See: **Conversion technology – Injection pressure**]. When semi-crystalline polymers such as polypropylene are subjected to shear as they cool crystallization may sometimes occur prematurely. This is illustrated in Figure 19, which contains a series of viscosity/shear stress plots over a range of temperatures. The onset of the phenomenon is manifest by a sudden upturn in the plot, from which it may clearly be seen that the temperature at which it occurs increases with the level of shear stress.

As explained when discussing the technology of injection molding [See: **Injection speed and Melting and solidification**], the onset of shear-induced crystallization will often result in brittleness where none would normally be expected.

Polypropylene resins containing higher than normal levels of crystallinity (mentioned above) are sold under the trade name *Adstif*, and exhibit very high rigidity, similar to those of some of the toughened polystyrenes and PVCs. In addition components produced from these materials have demonstrated improved gloss and surface hardness, coupled with better resistance to high temperatures. They are available in all three formats – homopolymer, heterophasic copolymer and random copolymer.

Figure 19: Shear-induced crystallization





## I Molecular mass and melt flow rate

The size and length of the growing chains are routinely manipulated during the various polymerization processes, and in this way a range of grades exhibiting differing molecular masses are produced. The importance of molecular mass, and its affect on flow in the mold has already been discussed elsewhere in this brochure. Information on the other properties controlled and influenced by this parameter is provided below.

Before moving on however, in practice the molecular mass is rarely expressed as such because the test used for its determination is complex and time consuming to operate. For convenience therefore it is usually expressed as the melt flow rate (MFR), the two parameters being related inversely.

Changes to the melt flow rate have implications for both the conversion interface and for end-use performance. As the MFR is increased

and flow in the mold is enhanced, both the primary and the secondary injection pressures become more efficient. In addition, mold packing is also enhanced, and so overall levels of shrinkage are reduced. In terms of physical and end-use performance properties rigidity increases with increasing MFR, but abuse resistance and impact strength decline. In addition, as the MFR is increased and the molecular chains become shorter, chains adjacent to each other can crystallize more readily. These relationships are shown diagrammatically in Figure 20.

To avoid any possible confusion, a trend-line for creep (important for large, load-bearing components such as crates and boxes) has been intentionally omitted from the above figure. Resistance to creep (as distinct from creep itself) increases with increasing MFR and reducing molecular mass.

## I Molecular mass distribution (MMD)

The manipulation of the growing chains mentioned above does not result in grades exhibiting a single value for the molecular mass, but rather a range of values that are distributed about an average.

Regular Ziegler–Natta polypropylene resins usually have a medium to broad width of distribution, and the majority of grades available on the market are of this type. However, the width may be changed during the production of the polypropylene, and in particular there are a number of important advantages to be gained from its reduction. Consequently, individual grades of polypropylene should be further characterized by reference to this distribution - either regular (as in the majority of cases), or narrow (also known as **controlled rheology** or **CR grades**). The width of the distribution affects both molding and end-use performances, as shown pictorially in Figure 21.

At an equivalent melt flow rate, as the width is reduced the response to shear in the mold (shear sensitivity) declines somewhat, and so such grades flow slightly less effectively. On the other hand, they exhibit enhanced resistance to warpage. At the same time their impact resistance tends to improve, but rigidity declines. However, it should be stressed that all of these effects are relative, and only really become significant when the distribution is particularly narrow.

More significantly, the molecular mass distribution is also affected by the nature of the catalyst used during polymerization. In particular, LyondellBasell's *Metocene* polypropylene products exhibit a particularly narrow distribution, and this topic, together with the implications arising is explained in greater detail below, when discussing the influence of the type of catalyst used.

Figure 20: Influence of melt flow rate on selected physical properties

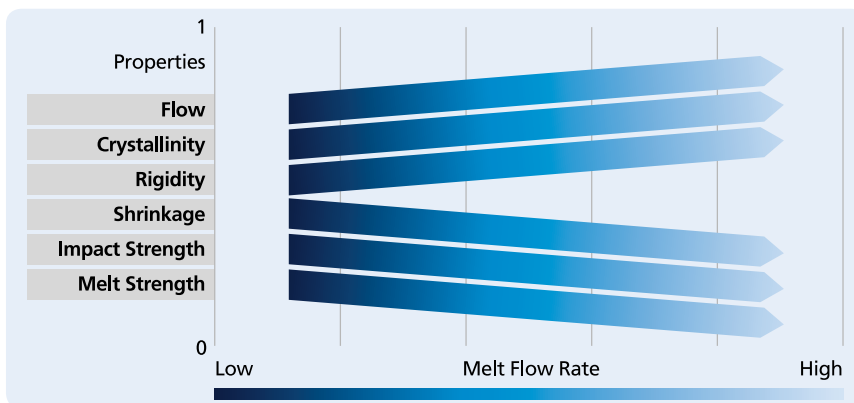
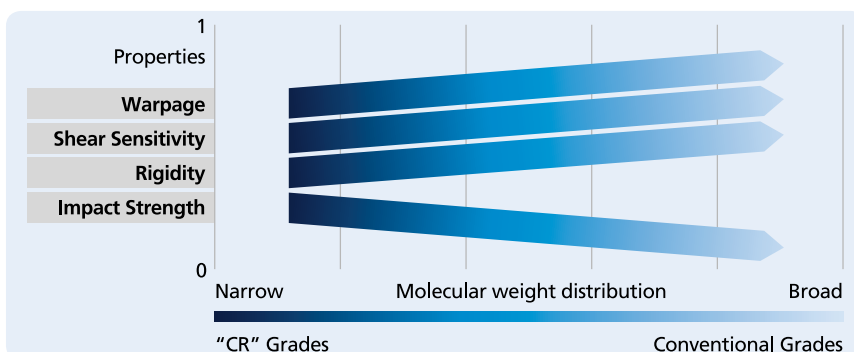


Figure 21: Influence of molecular mass distribution



## I Presence of selected additives

This part of the brochure provides advice on the effect of the addition of antioxidants and stabilisers, nucleants, clarifiers and antistatic agents - additives that are variously incorporated by LyondellBasell at the point of manufacture.

However, whereas the antioxidants and stabilisers are added to all polypropylene resins, nucleants, clarifiers and antistatic agents are added on a strictly "as-needed" basis. In addition,

### • Antioxidants and stabilizers

As a family of polymers the polypropylene resins perform best when antioxidants and stabilizers are incorporated into their formulations in order to protect them against thermal degradation during conversion – a procedure that has been established ever since their invention in the 1950s, and which fully complies with the requirements set-out by the various regulatory bodies.

Long-term oxidation in polypropylene (and in polyolefins generally) proceeds in exactly the same way as in any other organic substrate - by the generation of free radicals, by subsequent oxidation (addition of oxygen) and then by the exponential propagation of the reaction.

The free radicals have to be stopped at an early stage, and this is the role of the antioxidant. In structural terms they typically contain what is known as a hindered phenol group, and they work as scavengers for the free radicals. Another important property that these antioxidants must exhibit is thermal stability. They have to be able to survive the polymer converting temperature (i.e. 200°C and more), after which they still have to retain their effectiveness and be able to work during end-use (usually at room temperature, but in practice anything between around -30°C and +100°C).

The role of the stabilizer can also be that of a radical scavenger, but more commonly they are used to decompose the hydro-peroxides that are generated by the addition of oxygen to the carbon atoms within the polypropylene – in this

these later additives can alternatively be added in situ by the converter, for example by the use of a masterbatch. However, dependant on the conversion process the resultant dispersion of the additive may not be as good as that achieved by the above "fully-formulated" route, and so some of the potential advantage may not be realized. This caveat is particularly relevant to high-speed injection molding.

way, halting the propagation of the reaction, again at an early stage. In addition, like the antioxidant a stabilizer must be able to react at the polymer converting temperatures.

Normally, both the antioxidants and stabilisers are present in an additive package, due to the different and synergistic role played by them both.

### • Nucleants and clarifiers

In addition to resulting in the smaller crystal size mentioned above, the addition of a nucleating agent causes a significant increase in rigidity, and this change can be translated into improved top-load performance. Many homopolymer and heterophasic copolymer grades contain such additives.

The addition of a nucleating agent also causes the re-crystallization temperature ( $T_x$  or  $T_c$ ) to increase, and the polypropylene to solidify and set-up more quickly. This change has particular implications for the injection moulding sector, bringing the possibility for reduced cooling times and increased overall outputs. However, some care may need to be exercised since increased rates of set-up can sometimes lead to a reduction in the efficiency of the after-pressure, leading to slightly increased shrinkage.

The degree of nucleation and the magnitude of the above effects vary with the type of nucleant and in particular with the size of the nucleant particles. A number of different nucleants are regularly used, but the most common ones are talc and certain metal salts.

Random copolymers are routinely clarified rather than nucleated. Furthermore, the type of additive used and the principal objective in its addition are different. Clarifiers are often organic in nature, and the main reason for their use is in the enhancement of clarity and transparency.

### • Antistatic agents

The presence of dust and dirt on the surface of any injection moulded article is generally undesirable, and particular so in the case of rigid packaging, where it may well create a most negative image of the packaged contents. Unightly materials of this type tend to be attracted to the surface by the presence of the relatively high levels of static charge that build-up during conversion and subsequent handling. Antistatic agents are designed to limit this tendency to attract dust and dirt.

They work by migrating to the surface and then forming a cohesive molecular layer. In many instances this layer is hydrophilic, and so it attracts moisture from the air, and it is this in turn that acts as an electrostatically conductive medium and helps to dissipate any static charges, thereby limiting the formation of dust patterns. However, exceptionally low relative humidity in the conversion area (for example, in the presence of air conditioning, or during winter time at low temperatures) may limit the efficiency of the antistatic agent.

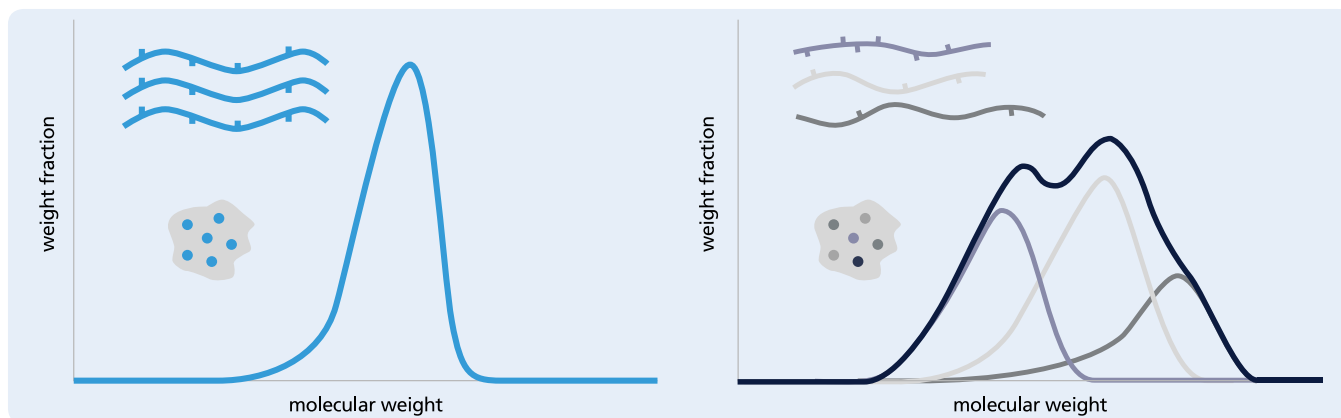


Figure 22: The effect of catalyst type on molecular mass distribution

## I Types of catalyst used during polymerization

As explained above in the brief summary on the manufacture of polypropylene, LyondellBasell uses two different catalyst technologies – namely Ziegler-Natta and metallocene. The polymers produced are all generically polypropylene, but they exhibit a number of interesting differences.

One of the most fundamental is in the number of so-called polymerization sites that are initiated during production. Polypropylene made by the use of Ziegler-Natta catalysts is comprised of a range of chains of different structures and different molecular masses, whereas the chains in those made with metallocene catalysts are much more uniform in structure and length. These differences are illustrated in Figure 22.

The manufacture, properties and performance of LyondellBasell's Ziegler-Natta based polypropylene have been established over many decades – they have a well-proven track record. However, metallocene-based alternatives have only recently

been introduced to the market, and so are likely to be less well-known. Consequently, the remainder of this section of the brochure concentrates on LyondellBasell's *Metocene* resins.

In their natural form many polypropylene resins tend to exhibit varying degrees of haze (even random copolymers), and this phenomenon is related to their semi-crystalline state. As light passes through the crystals it becomes slightly distorted and scattered, thereby giving rise to the somewhat opaque appearance. As mentioned earlier, with conventional polypropylene this limitation is often addressed by the incorporation of a clarifier, and in general terms this results in a reduction to the amount of scattering when the light passes through. However, *Metocene* crystals are smaller than those of conventional polypropylene. Therefore the resins are inherently less turbid to start with, and so when this same solution is applied to them the affect is that much more dramatic. As a result, clarified *Metocene* random copolymer polypropylene is potentially the clearest polypropylene available.

The ease with which the melt flow rate of *Metocene* polypropylene may be controlled is related to a particular sensitivity exhibited during the polymerization process. In absolute terms melt flow rates of more than 1000 are readily produced. However, in terms of injection molding, and the thin-walled sector in particular, this is limited to no more than 150 or so – but in all cases achieved directly during polymerization, without recourse to the kind of supplementary manipulation classically associated with CR grades.

Many of the properties of *Metocene* polypropylene resins arise as a function of their increased molecular uniformity and the associated reduction to the width of the molecular weight distribution, together with the virtual absence of low molecular weight material. Each active site of the metallocene catalyst molecule polymerises each incoming monomer unit in much the same way as the previously polymerized units, and consequently the chains in *Metocene* polypropylene resins are much more uniform in structure and length.

Finally, more detailed information on the properties of LyondellBasell's *Metocene* polypropylene in injection molding applications are provided in a separate brochure entitled "***Metocene* - Resins used in customers' injection molding applications**", copies of which may be obtained from sales offices and technical centers.

### LyondellBasell's *Metocene* polypropylene resins are typically characterized by:

Exceptional clarity

Greatly extended melt flow rate range, without recourse to secondary processing

Enhanced resistance to distortion and warpage

Somewhat improved organoleptic properties

Somewhat improved gas barrier properties

Homopolymers exhibiting lower melting-points

## Other properties of importance for injection molded applications

In addition to the controlling parameters discussed above, there are a number of other properties that may be important to the overall performance of polypropylene – namely chemical, organoleptic and notch effects.

### I Chemical features

Generally speaking, polypropylenes exhibit good resistance to most common chemicals, are largely unaffected by stress-cracking, and offer an extremely useful balance of resistances to the migration of common gasses and moisture.

More detailed information is provided below. Before moving-on however, it is strongly recommended that expert advice is always sought before polypropylene is subjected to any chemical environment.

#### • Chemical resistance

Generally speaking, LyondellBasell's injection molding polypropylene is highly resistant to chemicals, essentially due to their hydrocarbon character and their structure.

Strong oxidising acids have been reported to chemically attack, whilst some other substances may cause swelling, but most have little or no affect. Full and comprehensive details are given in the LyondellBasell brochure "**Polypropylene chemical resistance guide**", copies of which may be obtained from LyondellBasell's technical centers and sales offices, and online at [www.polymers.lyondellbasell.com](http://www.polymers.lyondellbasell.com).

#### • Resistance to stress cracking

After exposure to certain chemical media, some polymers may form cracks when subjected to internal and external stresses below the yield-point, and suffer brittle failure. This is the phenomenon of stress-cracking, observed particularly in the presence of soaps and detergents, and made worse at elevated temperatures.

Unlike polyethylene, with a few well documented exceptions, polypropylene does not suffer from this phenomenon.

#### • Permeability

It is generally recognized that the barrier properties exhibited by polypropylene to the migration of water vapor/moisture are among the best of the common commodity thermoplastics. Resistance to the migration of oxygen is not quite so good, but none the less our customers report that it is perfectly adequate to meet the requirements associated with the packaging of products with only limited shelf-lives, such as yellow fats, yoghurts and creams etc.

To a limited degree polypropylene resins are permeable to certain gasses and vapors, such as oxygen, carbon dioxide and moisture. The efficiency of a molded polypropylene component as a barrier to the migration of these materials is thought to be related to the mobility of the molecular chains at the high-end of the distribution, and in particular to the presence or absence of relatively low molecular weight/mass chains through which they can move.

The theory suggests that this is the reason why those polypropylene resins with a reduced amount of low molecular weight/mass material (such as LyondellBasell's *Metocene* resins) exhibit slightly superior barrier characteristics. None the less however, the fact remains that LyondellBasell's regular Ziegler-Natta *Moplen* types already have a proven track record.

## | Organoleptic characteristics

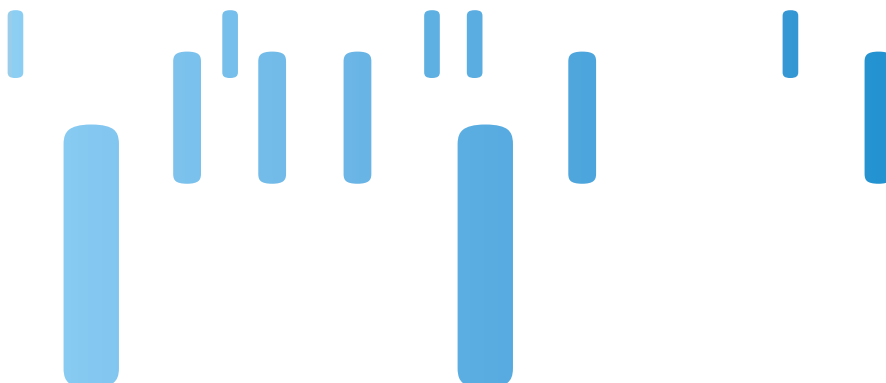
LyondellBasell is very conscious of the need to ensure that their polypropylene used in food packaging does not impart any taint or odor, and so the processes by which they are produced, together with the nature and type of any additives used are carefully screened. Once again the polypropylenes have an established track record.

Furthermore, in comparison with Ziegler-Natta polypropylene, the use of *Metocene* resins is reported to result in fewer taste and odor transfer problems with sensitive food. These properties seem in particular to be affected by the reduced amount of low molecular weight/mass material, and by the more uniform structure generally.

## | Notch effects

The phenomenon of notch sensitivity was introduced earlier in this brochure, when discussing component design [See: **Conversion equipment – Component design**].

The sharpness of any notch is well-known to exert a strong influence on impact performance, and a more reliable measure of the sensitivity may be obtained by determining notched impact strengths over a range of different notch-tip radii. Its effect varies considerably from polymer to polymer. However, polypropylene is by no means the most sensitive of common thermoplastics to this phenomenon.



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