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THE REACTOR GRANULE TECHNOLOGY: THE ULTIMATE EXPANSION OF POLYPROPYLENE PROPERTIES?

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Key Words: Polypropylene, Reactor Granule Technology, New Production Technologies

ABSTRACT

The progresses obtained in both catalyst performances and process technologies have made the continuous expansion of PP properties possible. The discovery of $MgCl_2$-supported catalysts and the development of their controlled spherical morphology produced a real revolution in the catalytic-system performances. A series of definitive improvements in catalyst chemistry and an impressive increase in polymer productivity were allowed by the total control of the "replication" phenomenon of polymer generated by the parent catalyst. The Reactor Granule Technology started up with relevant consequences in terms of development of new polymer properties for new applications and new markets, and of new economic and versatile process technologies with the best environmental impact. Through this technology, it is also possible to use a mixed catalysis combining the heterogeneous Ziegler-Natta catalysts with homogeneous catalysts such as radicalic initiators, metallocenes and single site, and this possibility results in a dramatic development of the material potentials and properties. The recently conceived "Multizone Circulating Reactor Technology" represents the ultimate frontier in the polymeric materials science. It will allow the uniform

phase homogenization of dissimilar materials generating novel polymeric alloys with an enormously expanded property/performance envelope.

INTRODUCTION

Even though the production of polypropylene (PP) only started in 1957 (only three years after its discovery [1-2]), its commercial success has been so wide that today the world-wide consumption of PP has reached 25 million tons/year (Figure 1) and an expansion of 5.9%/year to 30 million tons is forecasted for the year 2002.

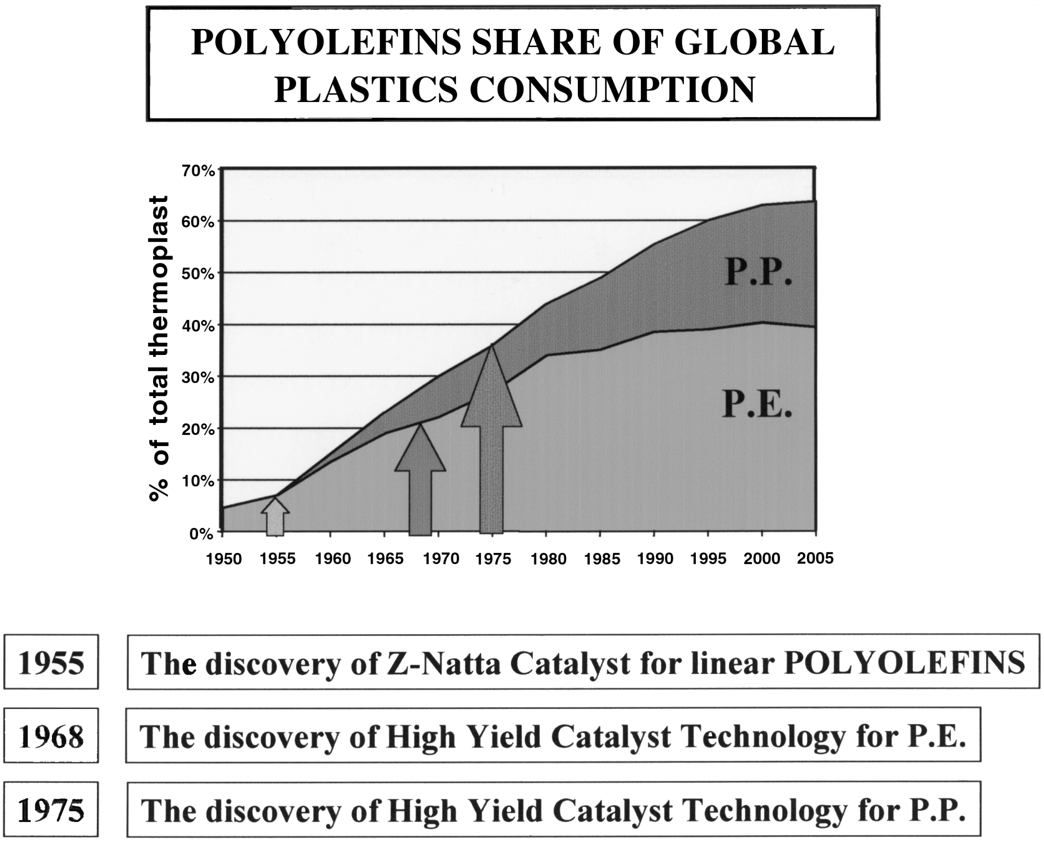


Figure 1. The fast growth of PP and PE determined by high yield supported catalysts.

This is the highest growth related to the major thermoplastics and only polyethylene production will have a comparable increase. The main reasons for this expansion are essentially due to the impressive development of technologies and to the widening of PP properties we have had during the years. Few materials in man's history have found as many applications as PP. PP is present in very different sectors: flexible and rigid packaging, medical, housewares, fibers pipes, wires and cables, coating, automotive, appliances, garden furniture, consumer goods, geotextiles, and geomembranes, etc… Its commercial growth and popularity is not fortuitous but is based on a favorable cost/property/perfor-mance balance.

It is well known that in the period 1988-98 the increase of PP consumption in Western Europe resulted from its introduction in sectors previously held by other plastic or traditional materials.

The second revolution in Ziegler-Natta (ZN) catalysis and in the polyolefins industry was due to the discovery and the implementation of the "Reactor Granule Technology" (RGT) [3] in 1982. The industrial impact of RGT is well represented by the Montell starting up of a number of versatile production processes such as Spheripol, Catalloy, and Spherilene.

The most recent development of an innovative catalytic system represented by the mixed catalysis (Multicatalyst Reactor Granule Technology = MRGT) [4] and the latest born Multizone Circulating Reactor Technology (MZCR) [5] have tremendously expanded the applications of homopolymers, copolymers, and other polyolefin-based materials (Hivalloy) in all the sectors where other stiff, tough, resilient, soft and flexible materials can be substituted.

Catalytic System Development

Starting from Natta's discovery, the studies related to the catalyst made a continuous improvement in terms of yield (Figure 2) possible, the fundamental stages of which are reported in Table 1. An impressive growth of new PP-based polymers (Figure 3) was achieved at the same rate. Such a dynamic commercial development has been, and still is, due to a very intense and timely integrated R&D and Business line synergic cooperation. It succeeded in understanding the polymer properties the market needed, to create and to put on the market the new technologies, products and properties in the fastest way.

These products with improved properties (Figure 4) went to sectors where the simple crystalline PP did not have room.

The first important breakthrough was obtained in the late 60's:

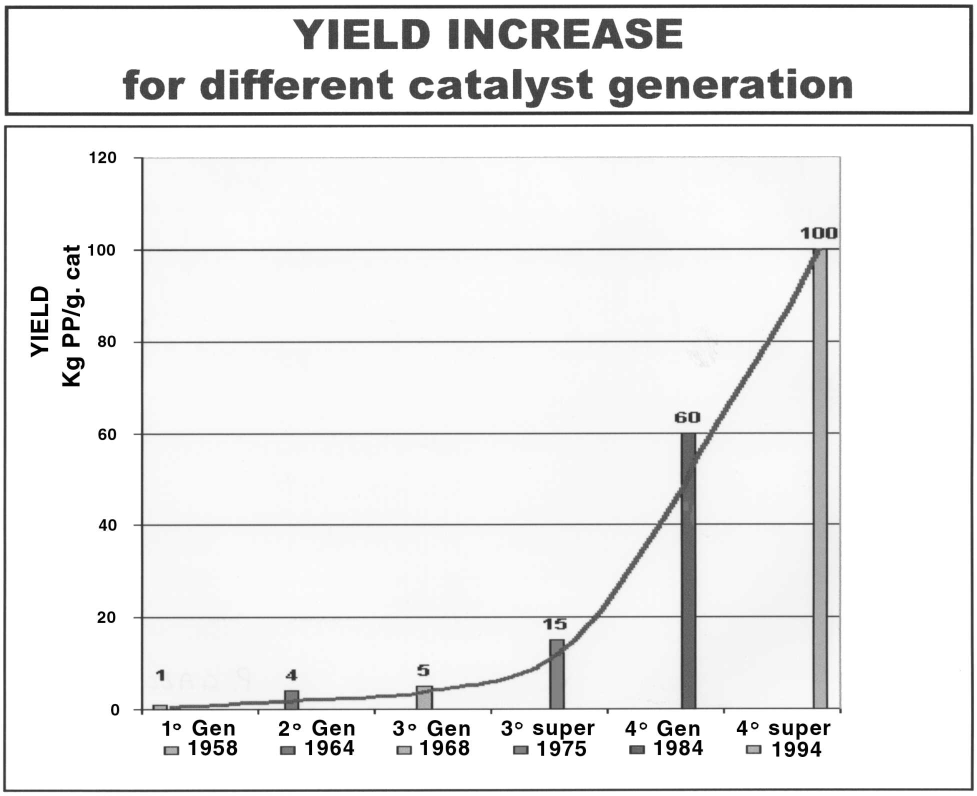


Figure 2. The relative yield improvement.

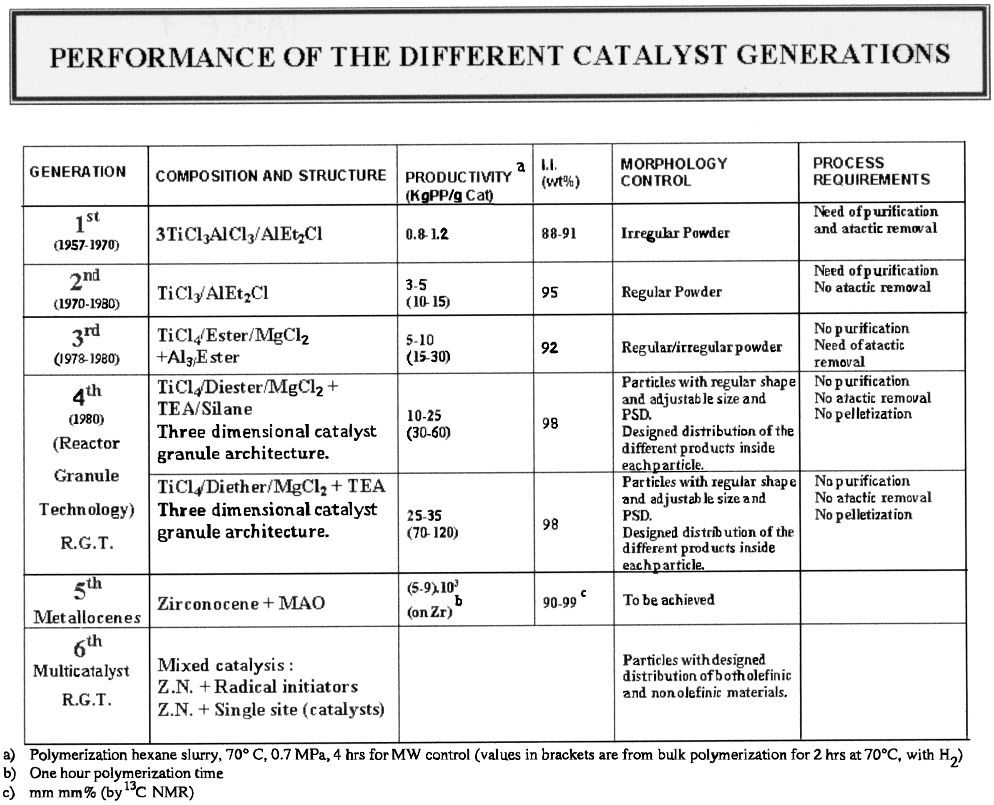
The discovery of the high activity and high selectivity $MgCl_2$-supported catalysts [6] brought about the elimination of the need of atactic fraction and catalyst residues by product removal with a significant simplification of the polymerization processes; the elimination of these constraints allowed a remarkable reduction in investment costs and several new degrees of freedom.

From this discovery, the "dream" of the "Ideal Catalyst" as extreme target in the heterogeneous catalysis was developed.

The idea was to obtain a catalyst having:

- very high activity and selectivity;
- control of polymer microstructure (MW and MWD chain shape, ran domness microtacticity);

TABLE 1. Milestones in PP Catalyst Development



PERFORMANCE OF THE DIFFERENT CATALYST GENERATIONS

GENERATION	COMPOSITION AND STRUCTURE	PRODUCTIVITY[a] (KgPP/g Cat)	I.I. (wt%)	MORPHOLOGY CONTROL	PROCESS REQUIREMENTS
1st (1957-1970)	$3TiCl_3AlCl_3/AlEt_2Cl$	0.8-1.2	88-91	Irregular Powder	Need of purification and atactic removal
2nd (1970-1980)	$TiCl_3/AlEt_2Cl$	3-5 (10-15)	95	Regular Powder	Need of purification No atactic removal
3rd (1978-1980)	$TiCl_4$/Ester/$MgCl_2$ +Al_3/Ester	5-10 (15-30)	92	Regular/irregular powder	No purification Need of atactic removal
4th (1980) (Reactor Granule Technology) R.G.T.	$TiCl_4$/Diester/$MgCl_2$ + TEA/Silane **Three dimensional catalyst granule architecture.**	10-25 (30-60)	98	Particles with regular shape and adjustable size and PSD. Designed distribution of the different products inside each particle.	No purification No atactic removal No pelletization
	$TiCl_4$/Diether/$MgCl_2$ + TEA **Three dimensional catalyst granule architecture.**	25-35 (70-120)	98	Particles with regular shape and adjustable size and PSD. Designed distribution of the different products inside each particle.	No purification No atactic removal No pelletization
5th Metallocenes	Zirconocene + MAO	$(5\text{-}9).10^3$[b] (on Zr)	90-99[c]	To be achieved	
6th Multicatalyst R.G.T.	Mixed catalysis : Z.N. + Radical initiators Z.N. + Single site (catalysts)			Particles with designed distribution of both olefinic and nonolefinic materials.	

a) Polymerization hexane slurry, 70° C, 0.7 MPa, 4 hrs for MW control (values in brackets are from bulk polymerization for 2 hrs at 70°C, with H_2)
b) One hour polymerization time
c) mm mm% (by ^{13}C NMR)

- control of polymer macrostructure (phase distribution and morphology i.e. particle size, shape, porosity);
- control of polymer properties (broad range of applications).

The "virtuosity" of this "Ideal Catalyst" was reducing the process constraints to zero and maximizing the technology versatility so as to have a significant expansion of the product property envelope.

The electron donors played a key role in determining the performances of $MgCl_2$-supported catalysts and a number of them were investigated in order to obtain an increase in isotacticity and crystallinity.

This fundamental research led to the development of different catalyst generations; the 4th generation (Table 1) in particular, between 1978 and 1982, allowed the second and most important breakthrough:

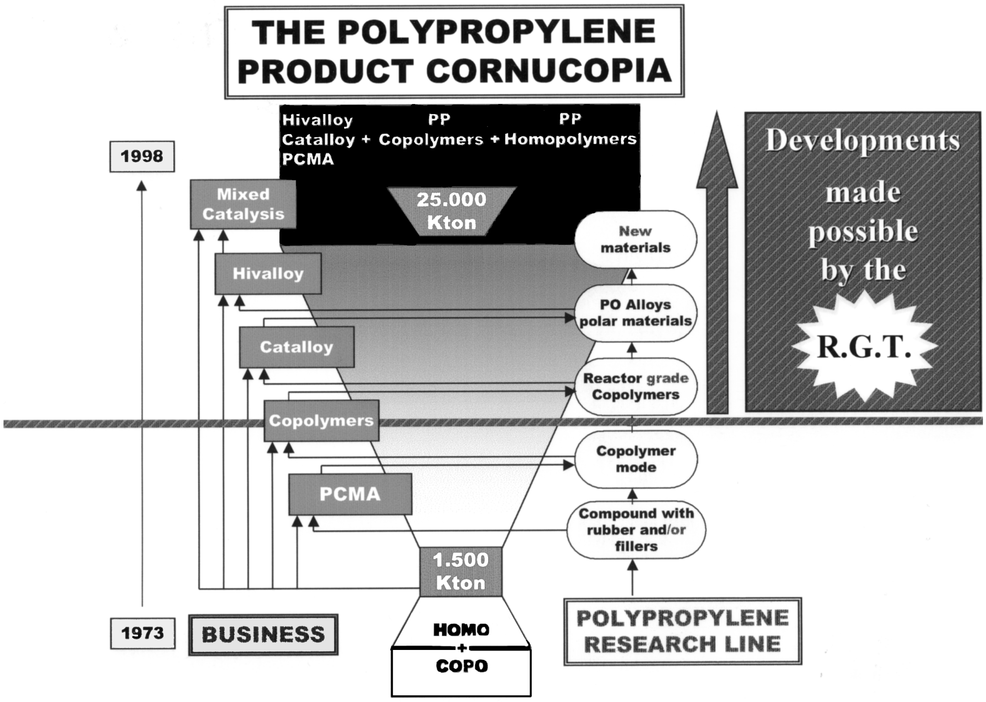


Figure 3. The effect of catalysts on the achievement of new "Polypropylenes".

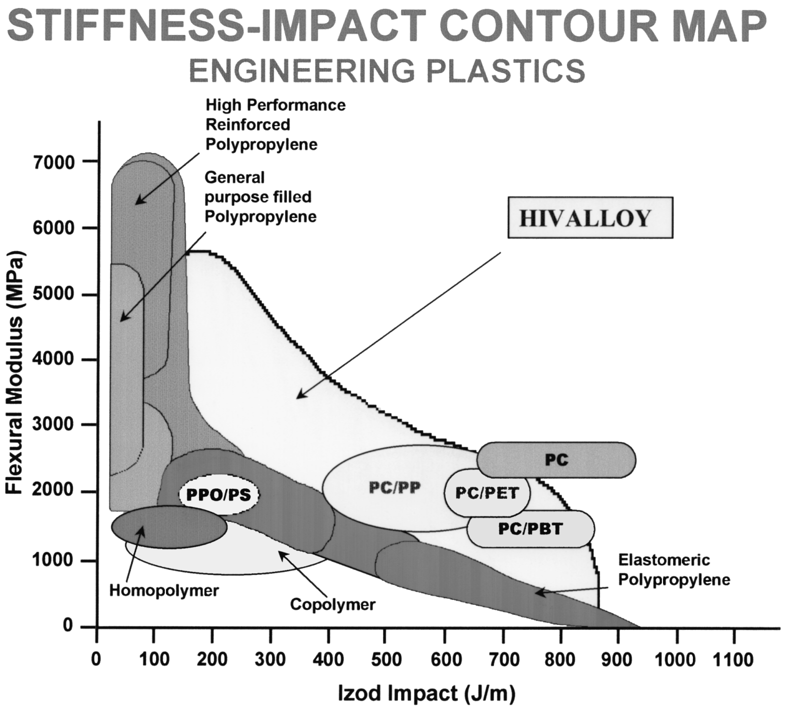


Figure 4. New rooms for PP-based polymeric alloys.

The Reactor Granule Technology (RGT) development, i.e., the scientific and technological impact of complete understanding and control of the catalyst-polymer growth mechanism.

It was observed that the morphology of the catalyst particle is completely replicated in the final polymer as particle growth takes place during the polymerization and this is confirmed also if the catalyst particles have a particular shape.

But the spherical form is the best to increase the flowability of polymers during processing, and for this reason, catalysts with controlled spherical morphology were developed allowing the full control of particle size and porosity of the related polymers (Figure 5).

The role of the *catalyst architecture* [7-8] in the controlled expansion of the polymer granule was explored in depth, so as to reach an optimum equilibrium between the mechanical strength of the growing granule and the catalyst polymerization activity [9-10].

Under appropriate polymerization conditions, polymer particles with an internal morphology ranging from compact to porous [11] can be obtained (Figure 6).

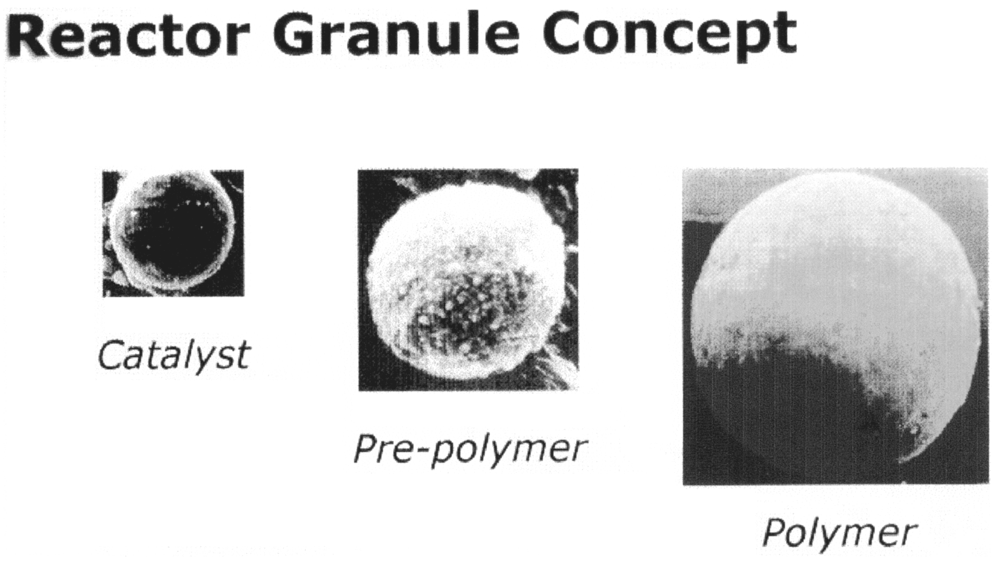


Figure 5. "Replication" phenomenon during the polymerization.

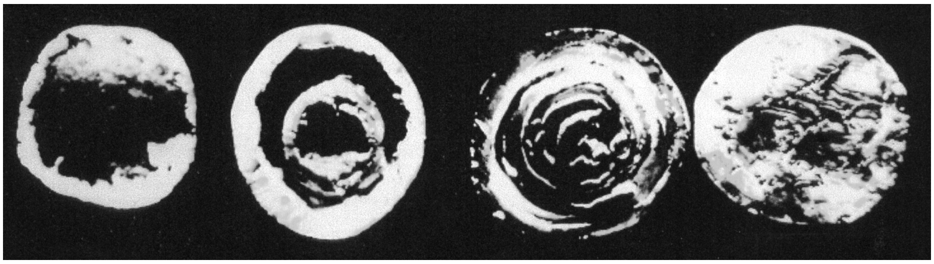


Figure 6. Different polymer morphologies from RGT.

The polymer particle has become the reactor itself in which polymerization occurs, and by changing monomer it is possible to obtain another polymer intimately dispersed within the mass of the solid granule of the matrix.

The process makes it possible to generate multipolymers, multiphase alloys and blends directly in the reactor, improving, and expanding the polymer property envelope, and creating really novel materials not achievable with traditional technologies.

As a consequence, new polyolefin production processes i.e., Spheripol (1982), Catalloy (1990), and Spherilene (1994) were developed.

New Production Processes

The possibility to obtain polymer particles having:

- Perfect spherical shape
- Narrow particle size distribution
- High bulk density
- Controlled degree of porosity
- Controlled internal morphology
- High process flowability

permitted us to maximize the operability of production plants reducing investment and running costs dramatically.

The slurry processes were improved, gas-phase reactors were explored, and the quality of polymers was optimized.

The industrial impact of RGT is well represented by the implementation of modern technologies like Spheripol, Catalloy, and Spherilene.

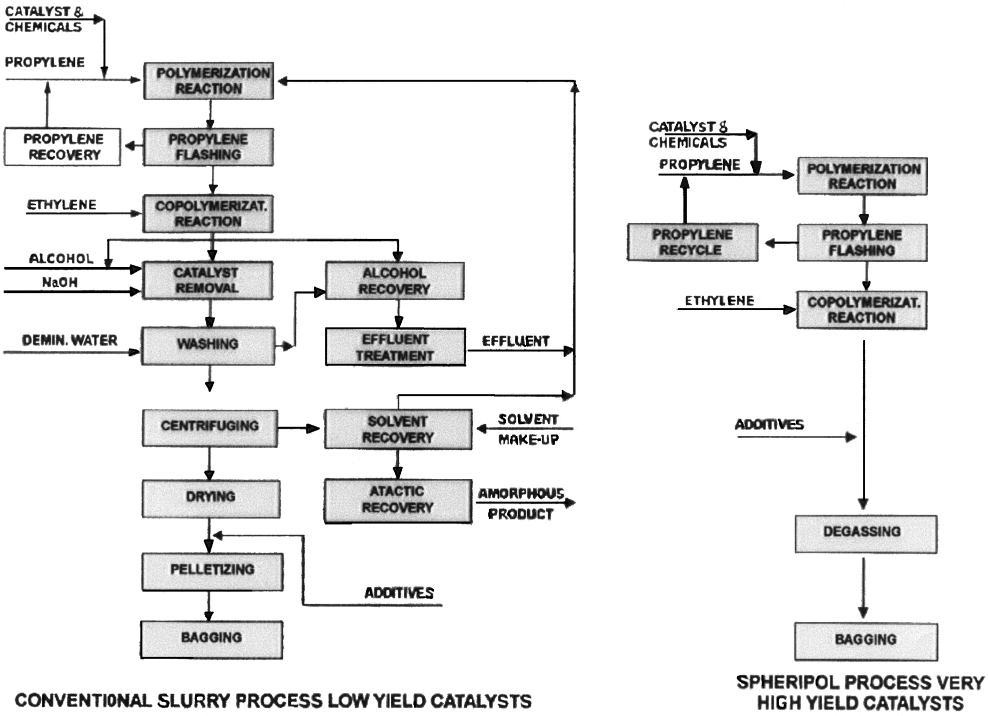


Figure 7. Technological evolution of the PP production processes.

The Spheripol process, using high yield catalysts, does not require the expensive purification section previously used to eliminate atactic fraction and catalyst residues; this allowed us to conceive a new process technology, completely eliminating the environmental hazards linked to the total absence of effluents but, most important, with a high versatility in terms of new products achievement.

This induced considerable simplification of the process (Figure 7) and reduction of investment costs (Figure 8).

The success of Spheripol process is, in fact, determined by the following points:

- flexibility in producing both highly crystalline and amorphous polymers, and homo- and hetero-phasic polymers covering a broad range of tailor-made properties (Figure 9):
- efficient technology
- reduced costs

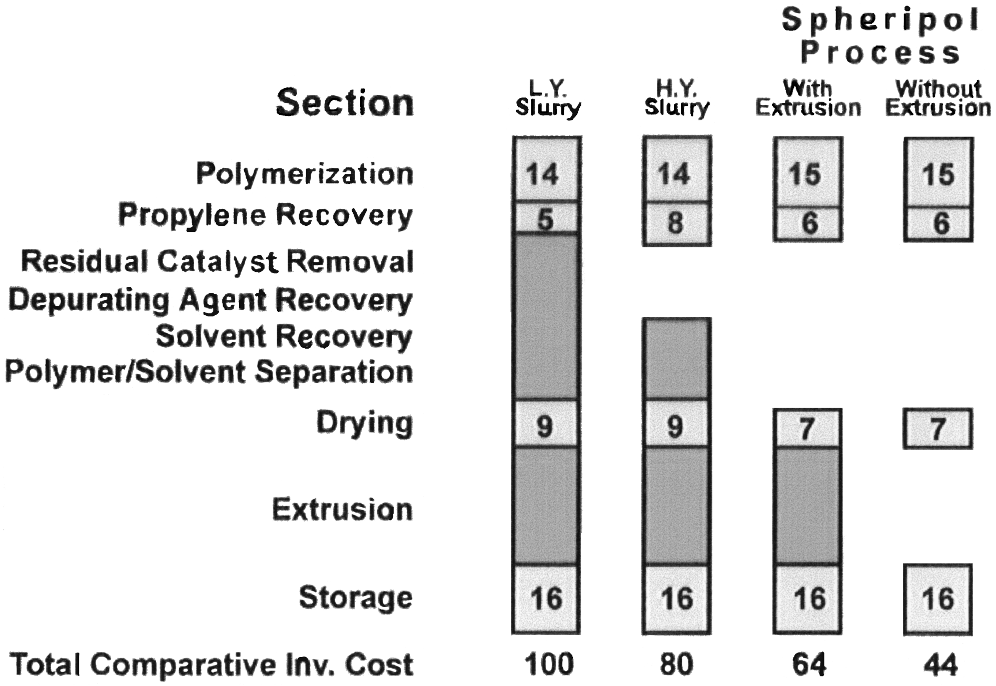


Figure 8. Polypropylene process evolution and investment cost comparison.

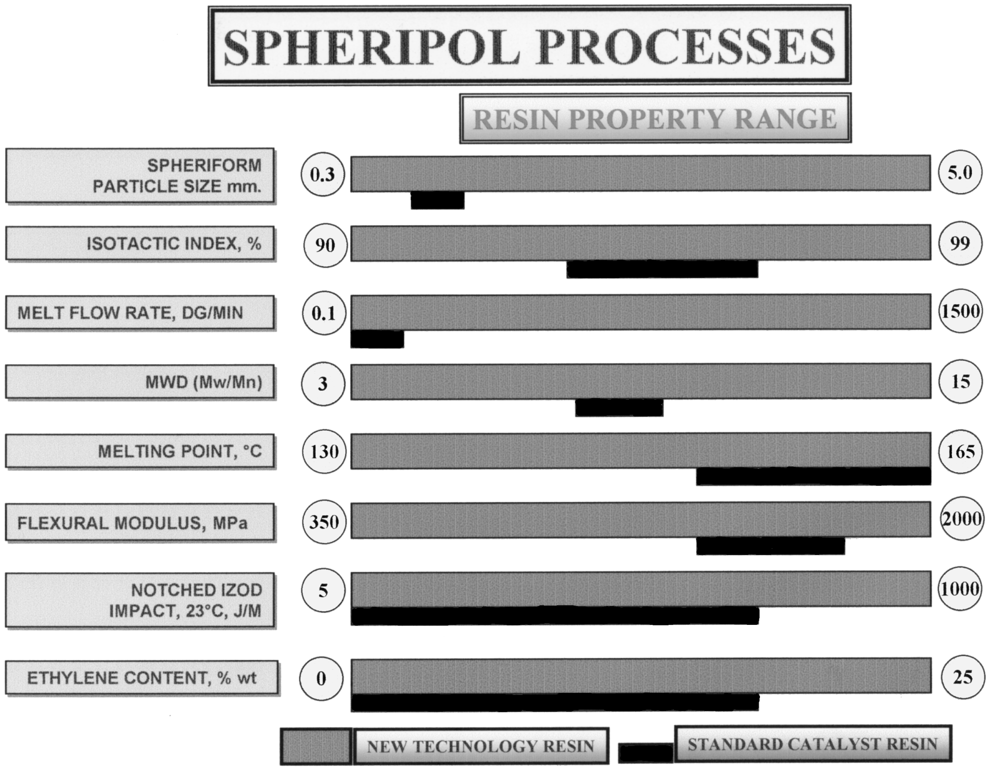


Figure 9. Spheripol process versatility.

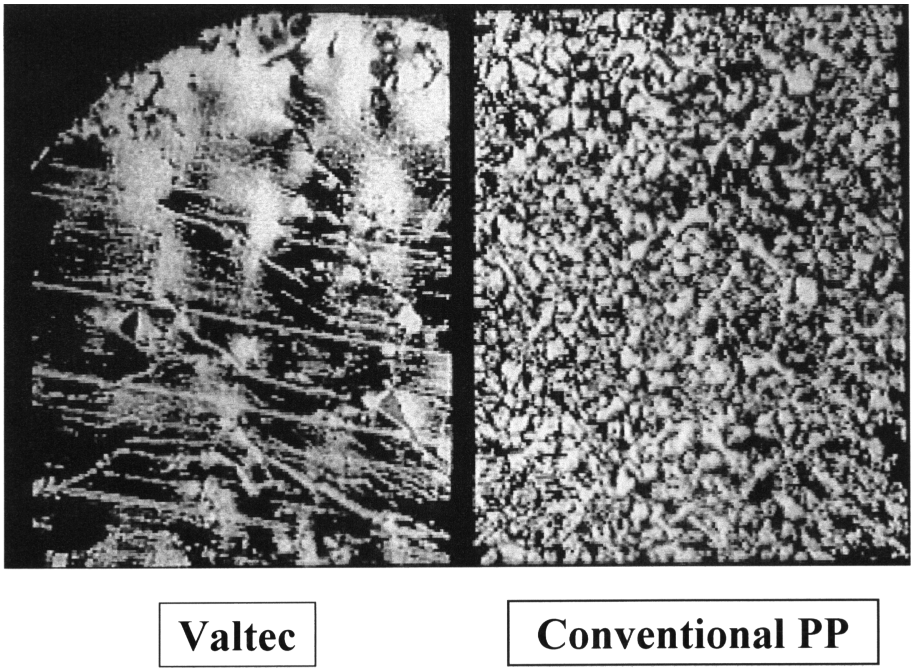


Figure 10. Electron microscope photography (magnification 300×) comparison between less developed structure of Valtec and more crystalline structure of conventional PP.

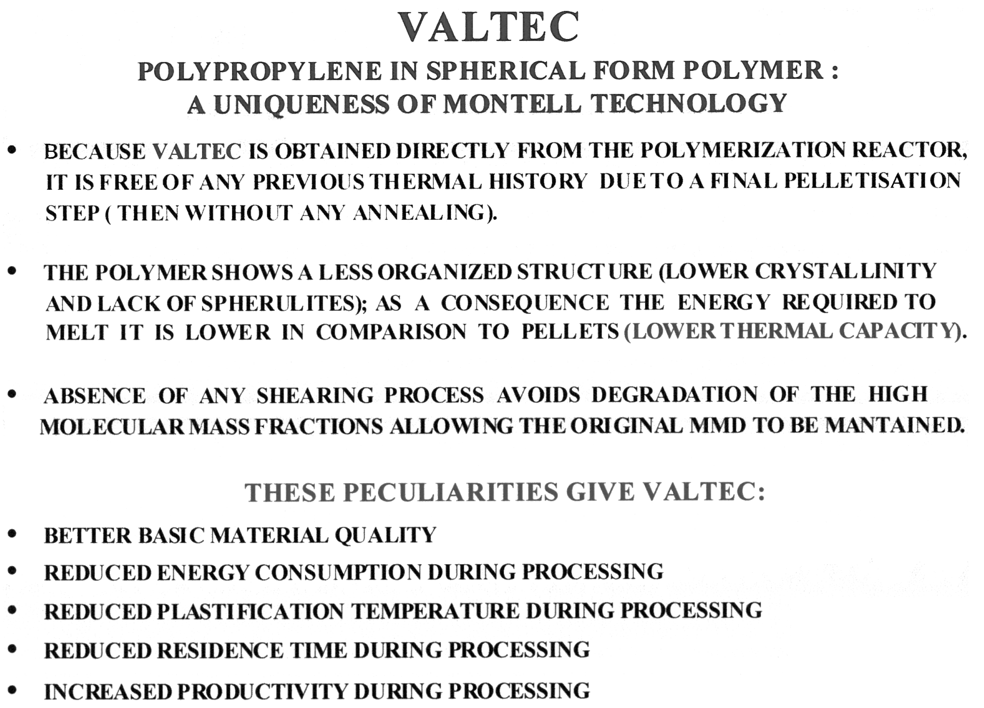
The most innovative and challenging version of the Spheripol process is called "Valtec"; it does not need the pelletization step (elimination of degradation risks) and is a perfect spherical replica of the catalyst which allows significant advantages for the customers in terms of:

- simpler addition of additives,
- reduction of transferring costs (sphere is the ideal shape for transportation),
- reduction of transformation energy costs (the spherical polymer has low crystallinity and then requires less energy to be melted) (Figure 10 and Table 2).

Spherilene is the technology implemented for PE production based on the same concept of "replication" phenomenon taken into account for Spheripol.

The Catalloy process is to be considered the maximum exploitation of the RGT because it takes advantage of the porous nature of the polymer particles

TABLE 2. Valtec Pecularities



VALTEC

POLYPROPYLENE IN SPHERICAL FORM POLYMER :
A UNIQUENESS OF MONTELL TECHNOLOGY

- BECAUSE VALTEC IS OBTAINED DIRECTLY FROM THE POLYMERIZATION REACTOR, IT IS FREE OF ANY PREVIOUS THERMAL HISTORY DUE TO A FINAL PELLETISATION STEP (THEN WITHOUT ANY ANNEALING).
- THE POLYMER SHOWS A LESS ORGANIZED STRUCTURE (LOWER CRYSTALLINITY AND LACK OF SPHERULITES); AS A CONSEQUENCE THE ENERGY REQUIRED TO MELT IT IS LOWER IN COMPARISON TO PELLETS (LOWER THERMAL CAPACITY).
- ABSENCE OF ANY SHEARING PROCESS AVOIDS DEGRADATION OF THE HIGH MOLECULAR MASS FRACTIONS ALLOWING THE ORIGINAL MMD TO BE MANTAINED.

THESE PECULIARITIES GIVE VALTEC:

- BETTER BASIC MATERIAL QUALITY
- REDUCED ENERGY CONSUMPTION DURING PROCESSING
- REDUCED PLASTIFICATION TEMPERATURE DURING PROCESSING
- REDUCED RESIDENCE TIME DURING PROCESSING
- INCREASED PRODUCTIVITY DURING PROCESSING

allowing a homogeneous distribution of high amounts of rubbery phase into heterophasic copolymers without reactor fouling problems.

A wide family of “alloys” became available by using different olefinic monomers ranging from superstiff to supersoft, enlarging the range of properties (Figure 11) in such a way to allow PP to compete and enter markets where other more sophisticated and expensive materials were dominant (Figure 12).

New Frontiers in Polyolefins

The latest possibility of the RGT has been to enter in the so-called “mixed catalysis” or “Multicatalyst Reactor Granule Technology” (MRGT) where a porous polymeric granule obtained through Ziegler-Natta heterogeneous catalysis can be impregnated by a homogeneous catalyst (radical initiator or single site) able to generate a new gamut of properties not achievable via Ziegler-Natta catalysts, so as to obtain a new final polymeric alloy having either

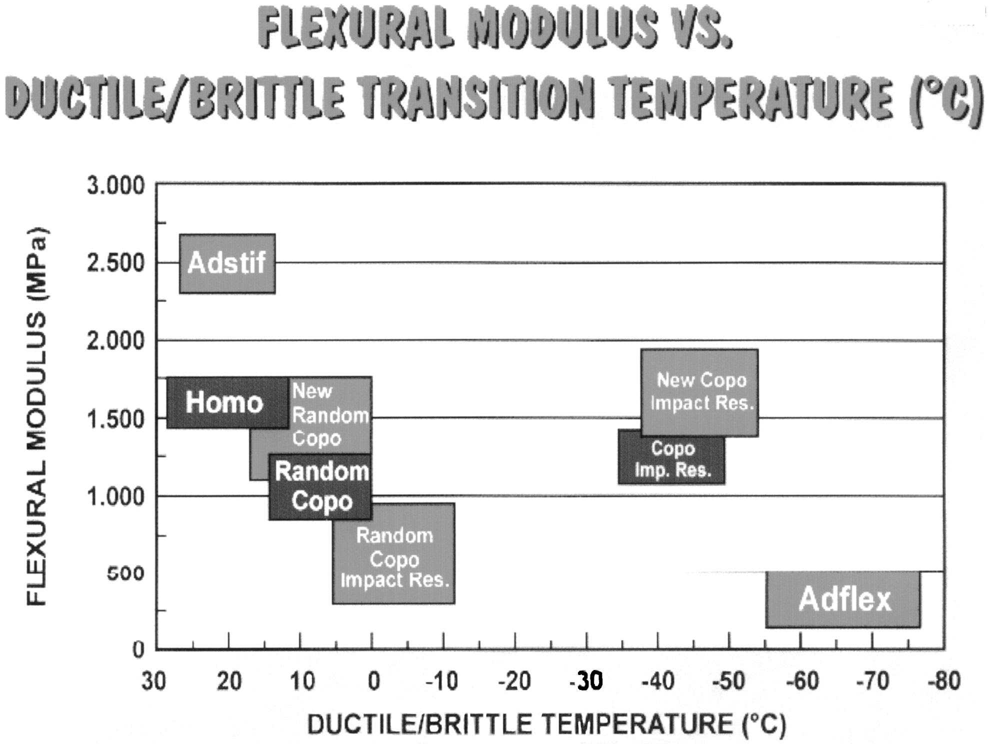


Figure 11. Expansion of properties due to Catalloy polymers.

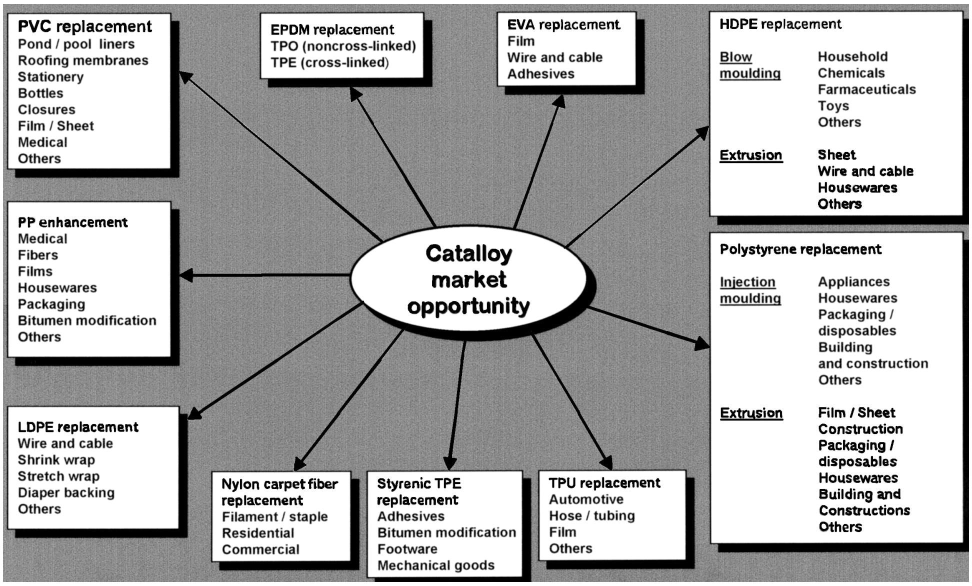


Figure 12. New application fields for Catalloy polymers. Catalloy's property overlap applies to several subsegments within the addressable markets identified.

improved mechanical characteristics in comparison with similar blends prepared by mechanical mixing, or generating a real novel material with new expanded range of properties not even achievable via blending.

The first example of mixed catalysis application has been the Hivalloy technology.

The introduction of non-olefinic monomers (styrenic, acrylic, etc.) into the polyolefin matrix through radical grafting has allowed us to obtain well-compatibilized materials having improved properties such as:

- heat resistance
- impact strength
- modulus
- scratch resistance
- gloss
- mold shrinkage
- low cycle time
- creep resistance

while maintaining other typical polyolefin properties, like:

- processability
- ductility
- chemical resistance
- weatherability
- weld line strength
- low production cost.

The Hivalloy polymers can expand the range of processability and flexural modulus beyond the limits of products obtained from other technologies (Spheripol, Catalloy) and can then compete in the application areas typical of engineering materials (Figure 13).

Metallocenes or other single-site homogeneous catalysts can be introduced into the granule of the porous spherical polymer obtained by Ziegler-Natta catalysis (Figure 14), and it is then possible to have “microreactors” able to perform further polymerization of olefins with the second catalyst family.

A homogeneous distribution of the single-site catalyst into the porous Ziegler-Natta PP microgranule is clearly a basic prerequisite to obtain a perfectly spherical, homogeneous, and compact polymer granule made of the most different polymer compositions.

These homogeneous catalysts are able to control *Molecular Mass, Molecular Mass Distribution*, as well as *Microstructure* (stereo- and regio-regu-

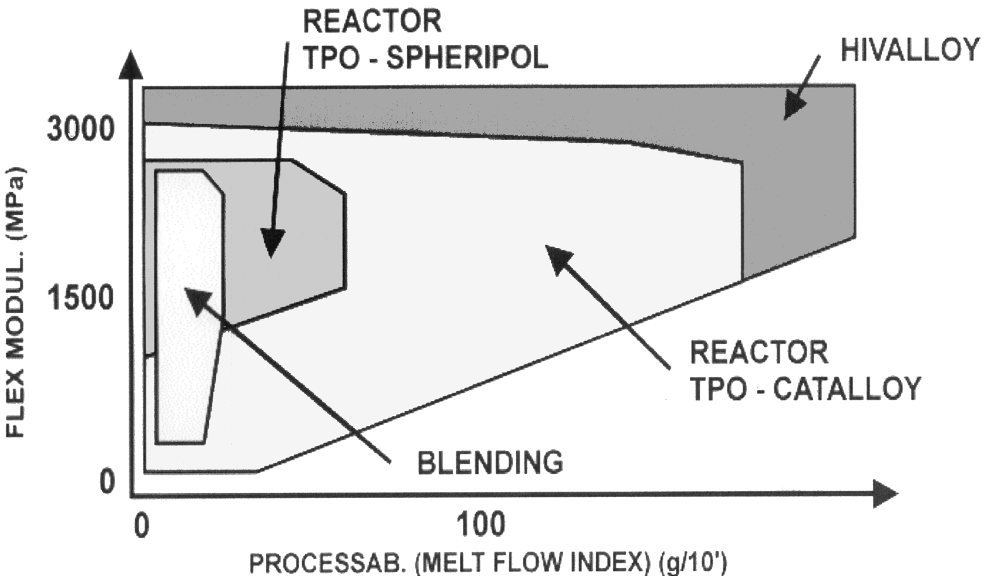


Figure 13. History of thermoplastic materials property envelope development.

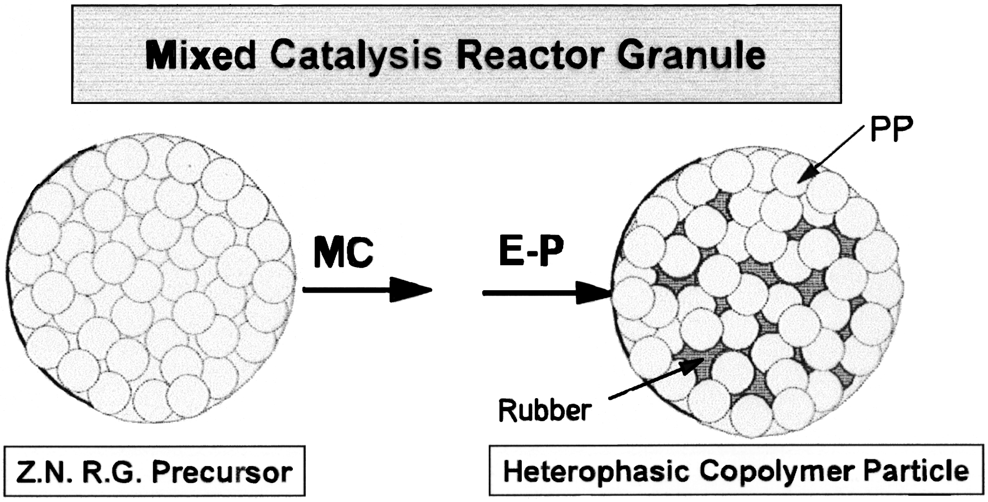


Figure 14. Impregnation of polymeric precursor with homogeneous catalyst.

larity and chain distribution of comonomers) in a wide range allowing us to generate improved or new polyolefin materials.

Their industrial application is extremely interesting.

The combination of polyolefin materials of different catalytic origin, such as Ziegler-Natta and single-site, has the potential of maximizing the property envelope of the final material achieving the best compromise among the different original properties

The polymers obtained are intimate blends of two different polyolefins in terms of structure and molecular mass and this suggests that an improvement in mechanical properties can be obtained in comparison with similar blends prepared by mechanical mixing.

The polymers prepared by mixed-catalysis combine the advantages of heterogeneous catalysts, like processability and versatility, with those of homogeneous catalysts, like physico-mechanical and elastic properties.

The best rubber quality provided by metallocenes allows to achieve the best compromise of the original properties: the maximum in impact resistance (with the minimum volume fraction) without a significant loss in flexural modulus (Figure 15).

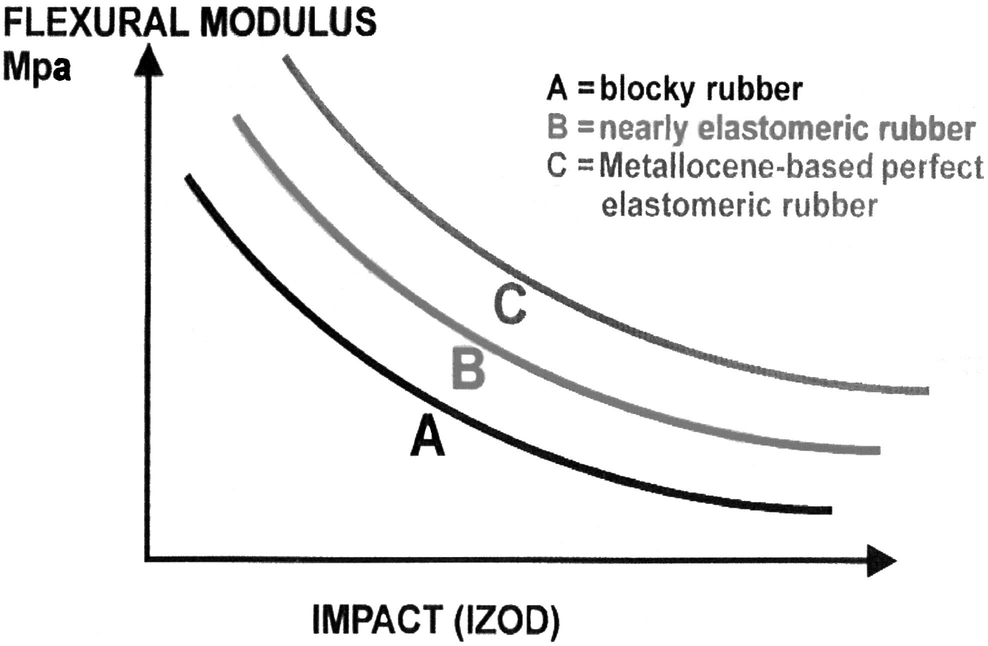


Figure 15. Flexural modulus/Izod impact balance as a function of volume fraction and nature of rubber.

With these last developments of RGT it is then possible to control:

- different compositions, structure and properties
- molecular mass and molecular mass distributions
- crystallinity of the homopolymer matrix
- composition of the second rubbery phase.

Unfortunately, the different polymeric phases produced inside the granule may result physically separated, inducing an insurmountable limit against the broadest expansion of the polymer properties envelope and the achievement of novel materials.

It is, for example, the case of all of the continuous processes with two or more reactors in series.

In the two or more steps, continuous process preparation of bimodal or bicompositional polymers, the polymer grain would consist of physically separated components.

This situation, especially if coupled with a large difference in molecular masses or in the degree of crystallinity, would clearly prevent effective mixing of the polymer fractions during melt processing and thus lead to finished articles with poor mechanical and optical properties.

In order to overcome these difficulties it is necessary to set up a continuous multi-stage polymerization technology capable of providing residence times per pass that are so short, so as to generate the different polymer components within the same shell or, if in different shells, making them so thin, so as to guarantee mixing at molecular scale.

With reference to the Broad Molecular Mass Distribution (BMMD) Polyethylene, as an example, the two cases are exemplified in Figure 16.

This principle has driven the research to the latest revolution in Montell technology, the Multizone Circulating Reactor (MZCR).

Starting from high yield catalyst, a stable pre-polymerized granule is obtained and is inserted in a reactor where it is subjected quickly and alternatively to different polymerization conditions (Figure 17).

In this way, it is possible to have a real intimate "compound" in the reactor, because the possibility to control size and location of the separated polymeric phases within the same polymer particle allows us to achieve a very homogeneous mixing also for dissimilar polymers.

Then the ability to produce and to intimately mix multipolymeric phases that are structurally different enables to expand the property/perform-ance envelope of polyolefins into non-olefinic regions and to create novel polyolefin materials with unique structure/performance properties.

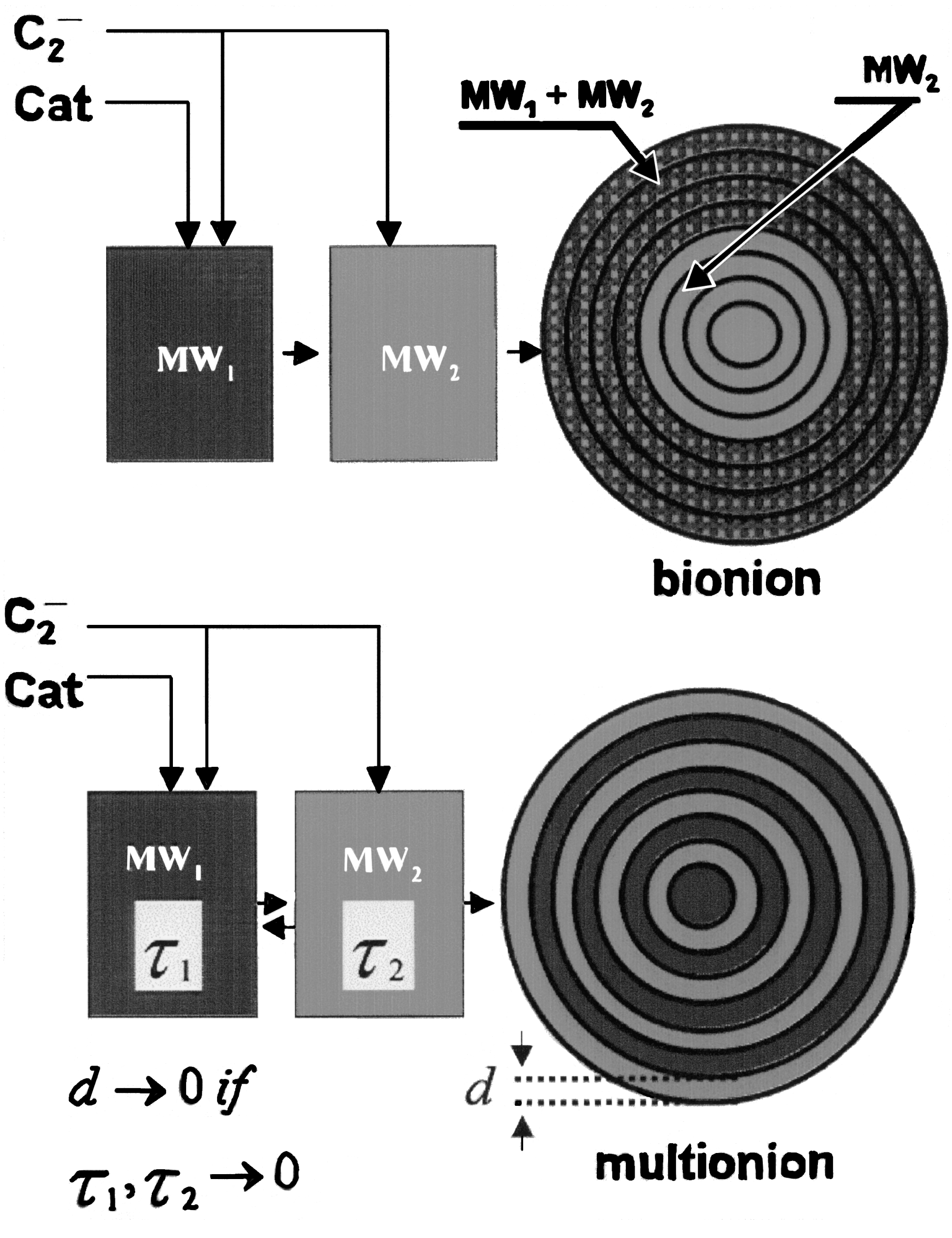


Figure 16. Expected morphologies of bimodal polyethylene grains: conventional two stage polymerization (top); Multizone Circulating Reactor Technology (bottom).

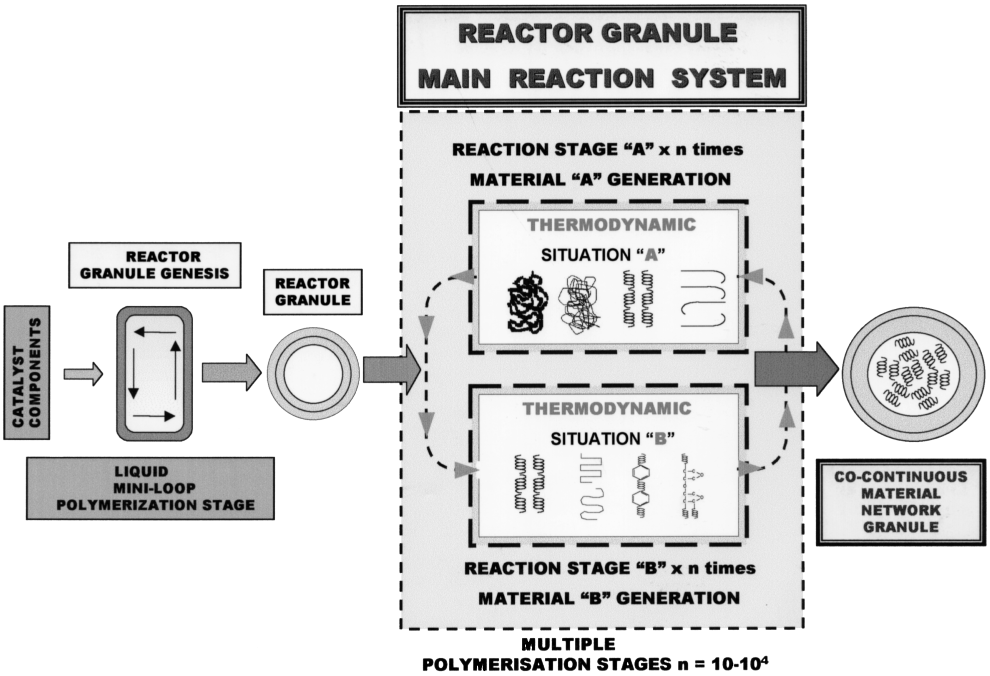


Figure 17. Working-principle of Multizone Circulating Reactor process.

Some examples of the potential of this new technology are reported as follows.

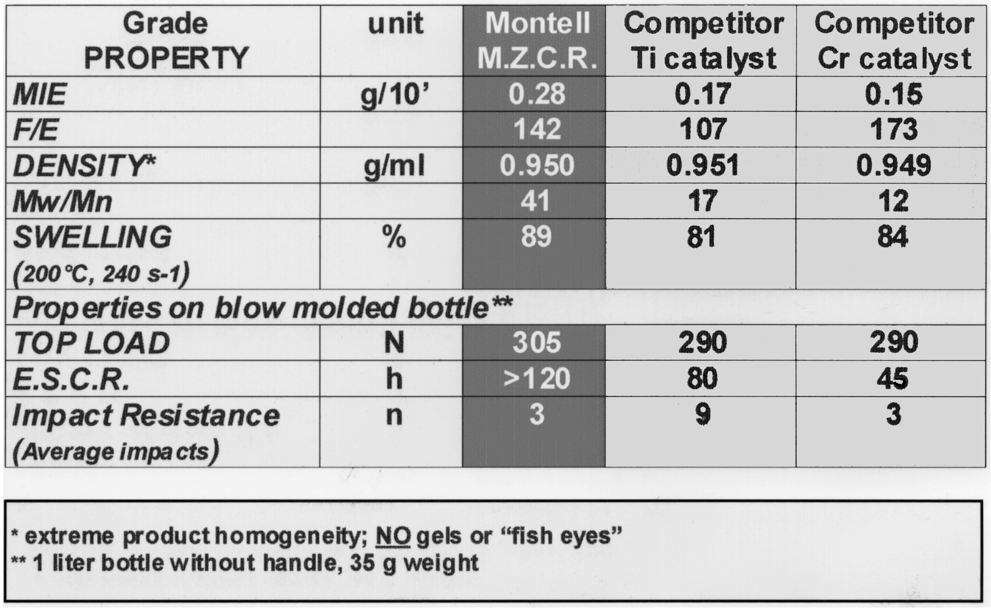
Polyethylene films have some limitations in their processability for the presence of gels (fish-eyes) due to the presence of high molecular masses not homogeneously dispersed.

Using MZCR technology, polyethylenes were produced with the same processability of the best product by competitors but with a very wide Molecular Mass Distribution, as reported in Table 3; films produced from such very homogeneous polymer do not contain fish-eyes at all.

The best polypropylene homopolymer from Spheripol technology (one reactor) has the characteristics reported in Table 4. The higher modulus obtainable is 1500 MPa.

Using the MZCR technology with one reactor the PP has higher isotacticity, wider polydispersity and a very high flexural modulus (2600 MPa). A product with a higher MFR shows only a slight decrease in the modulus value

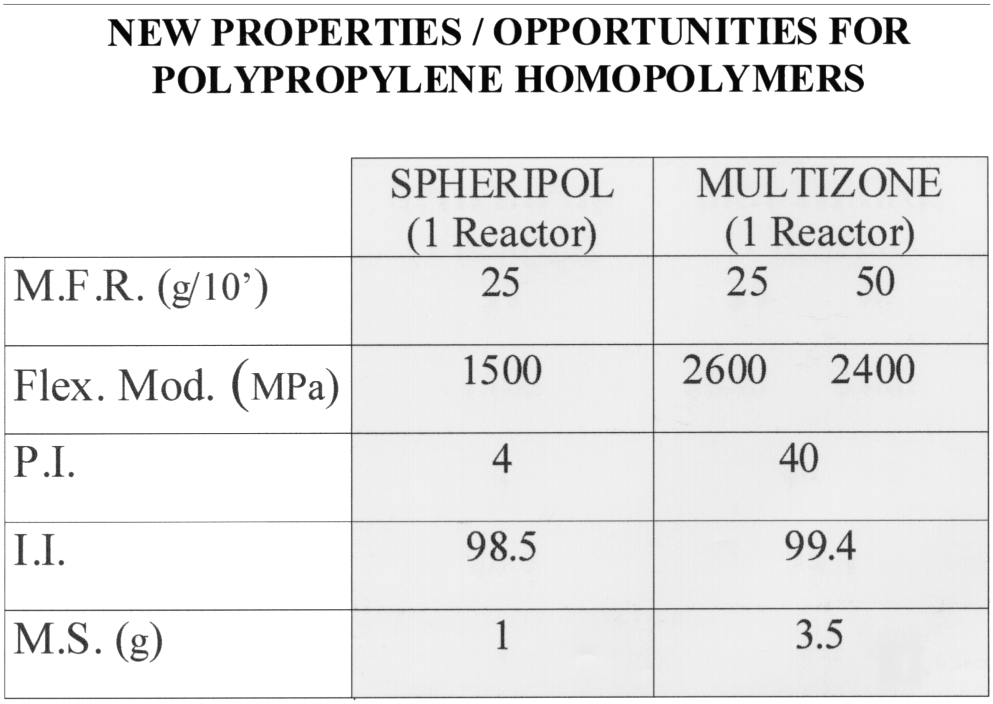
TABLE 3. Comparison of Polyethylenes Obtained with Different Technologies



Grade PROPERTY	unit	Montell M.Z.C.R.	Competitor Ti catalyst	Competitor Cr catalyst
MIE	g/10'	0.28	0.17	0.15
F/E		142	107	173
*DENSITY**	g/ml	0.950	0.951	0.949
Mw/Mn		41	17	12
SWELLING *(200°C, 240 s-1)*	%	89	81	84
*Properties on blow molded bottle***				
TOP LOAD	N	305	290	290
E.S.C.R.	h	>120	80	45
Impact Resistance *(Average impacts)*	n	3	9	3

* extreme product homogeneity; NO gels or "fish eyes"
** 1 liter bottle without handle, 35 g weight

TABLE 4. Comparison of Polypropylenes Obtained with Different Technologies



NEW PROPERTIES / OPPORTUNITIES FOR POLYPROPYLENE HOMOPOLYMERS

	SPHERIPOL (1 Reactor)	MULTIZONE (1 Reactor)	
M.F.R. (g/10')	25	25	50
Flex. Mod. (MPa)	1500	2600	2400
P.I.	4	40	
I.I.	98.5	99.4	
M.S. (g)	1	3.5	

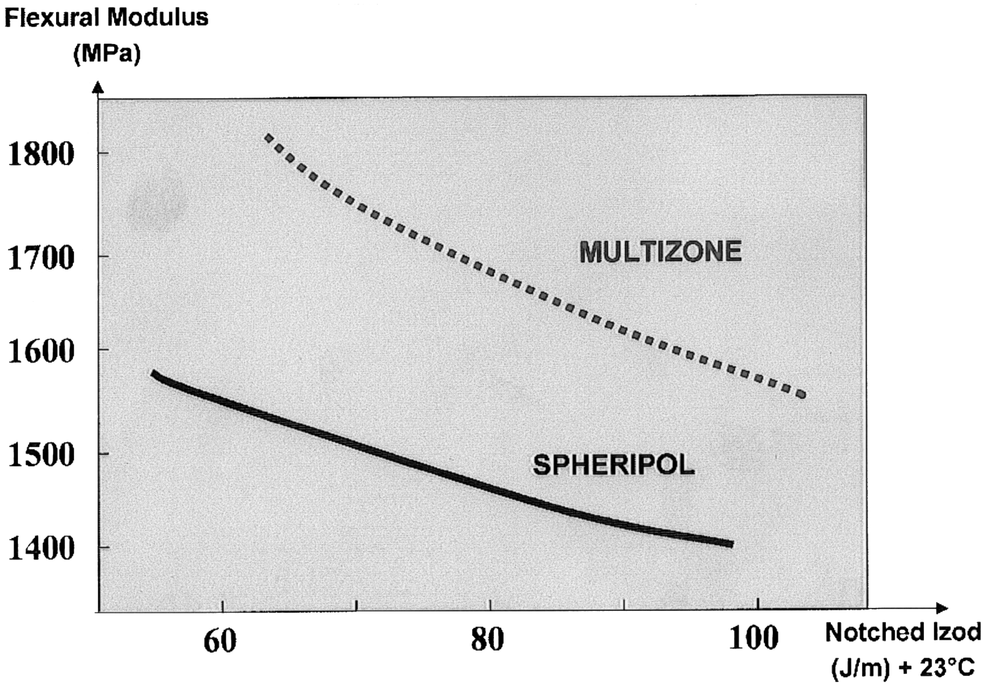


Figure 18. Comparison of heterophasic copolymers obtained with different technologies.

and this is a clear demonstration of the very intimate mixing of a very broad distribution of different molecular masses.

In the case of heterophasic copolymers, (Figure 18) it will be possible to improve the flexural modulus and the impact resistance at the same time producing a matrix with a very high isotacticity index and a perfectly dispersed rubber at very high molecular mass but totally amorphous.

The final morphology will really be like a “solid solution”.

The conclusion is that the potential of the MZCR is the best exploitation for PP and for polyolefins in general, allowing:

- A quantum jump in polyolefin properties expansion
- A dramatic simplification in processes being:
  - The new PE process/polymer frontier
  - The new PP process /polymer frontier
  - The best (the “unique”), the largest volume application route to the commercial exploitation of mixed catalysis (BMMD, copolymers)

- The novel process/polymer Catalloy model
- The "incompatible materials compatibilization"
- The "interpenetrated" polymer structure
- The "liquid crystal polymer" approach

CONCLUSION

Is PP over? What is it going to be?

The conclusion from the speech; "Polypropylene: 44 years young! The challenge from for the 21st century," Hamburg, September, 13-17 [12], can be quoted: **"The future is for PP at least as challenging as the past has been…….or even more"**

The reasons for this statement focus on the following two main points:

1) Polypropylene is still a young material with a very bright challenging future (Figure 19).

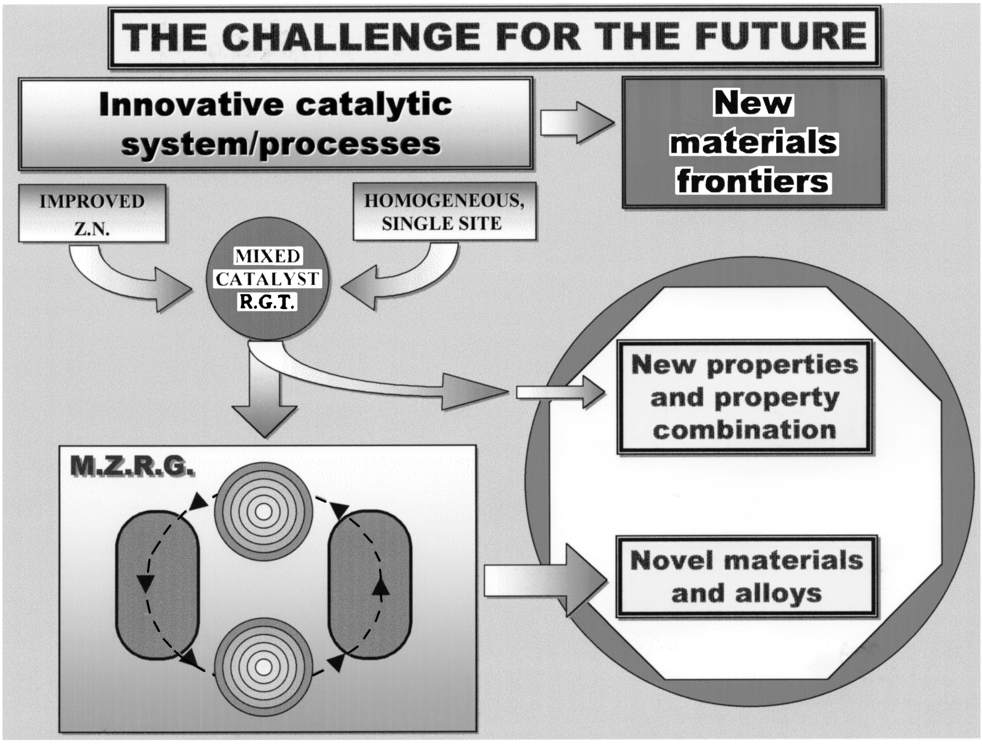


Figure 19. The future for PP.

It is possible, in fact, to generate completely new properties via innovative catalytic systems and to combine them in an *ideal* way via Multicatalyst Reactor Granule Technology (MRGT) and its ultimate frontier in terms of property combination, the Multizone Circulating Reactor (MZCR).

The dynamic development of technology will, in conclusion, allow us to improve and to always exploit better the most different polymer properties generated by the Ziegler-Natta and most of the homogeneous catalytic systems available for the olefin polymerization.

As a consequence, it will be possible to have a continuous and endless property expansion for the "new" polyolefin materials towards new polymer frontiers (Figure 20).

2) The Reactor Granule Technology (RGT) has opened the way to a generation of new families of polypropylenes via Spheripol process, polyolefin alloys via Catalloy process, polyethylene via Spherilene process, and Engineering Plastics via Hivalloy process.

It allows the generation and combination of different materials in the "Integrated System Approach" [13-14].

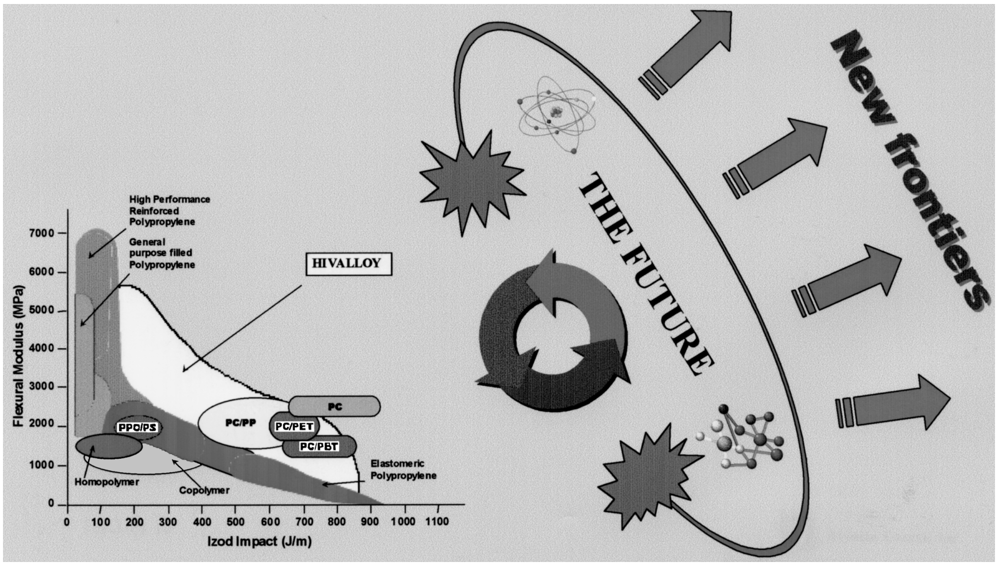


Figure 20. Expansion of PP properties. Afer the first 40 years from polypropylene commercialization, trends in expansion and generation of new properties continue to accelerate.

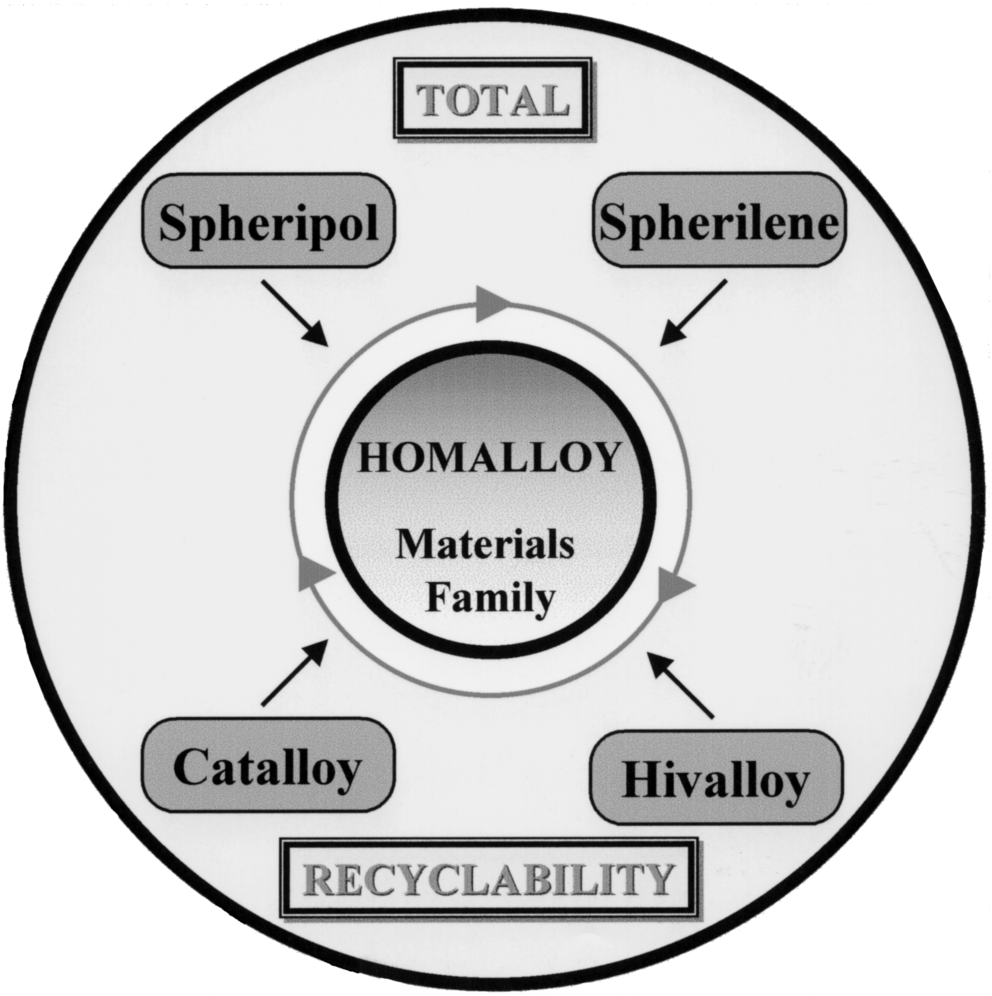


Figure 21. The total recyclability of PP based materials

It may be possible to create new application systems for polyolefin based materials, utilizing polymers with the most different final properties, and to make their recycling particularly easy because there is *no* need of any separation before recycling.

The final materials could be at the end considered, as "homoalloys" and could then be characterized by a complete recyclability (Figure 21).

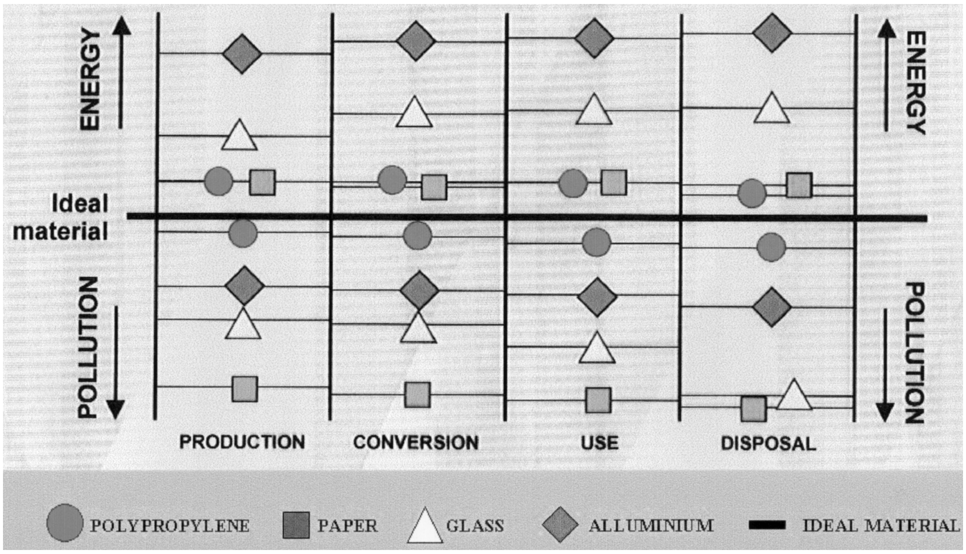


Figure 22. Comparison between "young" PP and old materials. This chart represents the eco-balance of polypropylene compared with other materials over their entire life span (no materials recycling) based on a meaningful interpretation of information from independent sources on packaging materials.

In addition to that, and also due to that, polypropylene has the best "green" image among the different materials due to its broad range of properties, its low production and processing costs and its very low environmental impact.

In comparison with PP, the oldest materials like glass, paper, and aluminum are more expensive and polluting; PP is near to be the "ideal material" (Figure 22).

Well, this "green" image will appear more and more with the new coming technologies that are able to combine industrial development with the protection of the environment for an effective improvement of the quality of life and its span.

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