# Polyolefin: Changing Supply-Demand Framework and New Technology

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**Summary:** Polyolefin industry is now under a remarkable change of international supply-demand framework and its market is splitting into commodity and high performance products. It is getting more important for a material being harmless and comfortable, while the "life cycle cost", which includes the cost during use and the recycle cost after use, is regarded as more important to evaluate a material. Those changes are accelerating the inter-material penetration. Several examples of the material design and production technologies, which responded to the changing market needs and developed new applications of polyolefin, are discussed.

**Keywords:** automotive application, composites, environment impact, metallocene catalysts, poly(propylene)

## Introduction

Polyolefin, combining polyethylene (PE) with polypropylene (PP), is the most broadly used plastic and its global production is estimated to have exceeded 80,000 kta in 2001. Recently, the supply and demand structure of polyolefin is remarkably changing. One of its major causes is the growing international competition of product supply. Gigantic global suppliers, which capacity is approaching 10,000 kta each, have emerged as the results of recent corporate consolidations. Meanwhile even the demand expansion in Asia Pacific area is not expected to absorb the ongoing capacity increase in that area including Middle East and China. Therefore, thorough cost reduction is essential especially for the polyolefin commodity products, to prepare the price competition anticipated in the near future. The improvement of polyolefin catalyst, which has been focused on the increase of catalyst efficiency and the development of efficient process, has largely contributed to reduce the catalyst cost and to eliminate the

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process of catalyst decomposition and neutralization. Several simplified processes, such as gas phase process, which doesn't need the solvent recovery facilities, have been also developed to reduce the utility cost (Figure 1).[1] As the results of those improvements, the raw material cost has become to dominate the manufacturing cost of polyolefin and is almost determining the profitability especially of the commodity business. Japan doesn't have the major resource of low cost materials and is still highly depending on the old manufacturing process due to the long history of polyolefin industry. Therefore, the development of the high performance product market is getting more important to maintain the profitability in Japan. Those changes in the polyolefin industry are expected to accelerate the business to be separated into two major directions, that is, the rationalization in the commodity area and the development in the high performance area.

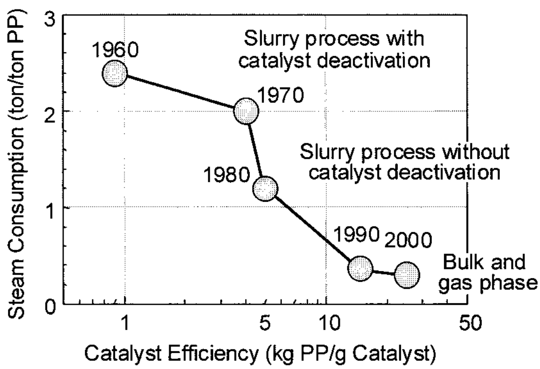
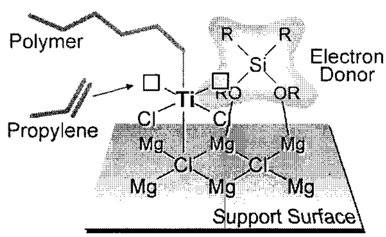



Fig. 1. Development trend of PP polymerization catalyst and process.

On the other hand, the market demand for polyolefin is also changing reflecting the recent transfiguration of social requirements, though there may be regional conditions. In Japan and several countries of North America and Europe, there is an increasing demand for the materials of environment friendliness, safety, convenience, comfort during use, and so on. The material cost is also being evaluated by "life cycle cost", which is the grand sum of all expenses including manufacturing cost, energy consumption during use, recycle cost after use, and environment impact. Those changes cause the recent inter-material penetration. Material design and production technologies are getting more important to provide the necessary products responding to the changing market demands. Several examples of new technologies, which expanded the applications of polyolefin, are discussed focusing on polypropylene.

## PP Molecular Structure Control Technologies

The two major first order molecular structures of PP are molecular weight and crystallinity, and the latter depends on the stereo regularity at the polymerization. The catalyst efficiency and the stereo regularity of PP have been remarkably improved to give the commercial PP materials with very high crystallinity, high stiffness, and high heat resistance at the lower cost. Those materials are now widely used in the industrial applications.



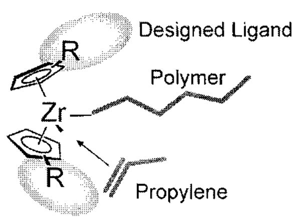




Fig. 2. Stereo regularity control models of propylene polymerization by Ziegler-Natta Catalyst (top) and metallocene catalyst (bottom).

Ziegler-Natta type titanium-based supported catalyst (Z-N catalyst) is most commonly used for the PP polymerization nowadays, but it has heterogeneity with the catalytic species and that provides by-product, or extractable fraction with the low molecular weight and low crystallinity. This fraction not only causes the lower strength and the lower heat resistance of PP material but also provides the several practical difficulties, for example, the fuming during processing and the odor of products. The largest factors to determine the stereo regularity of PP molecule are $MgCl_2$ support and the electron donor compounds, which are considered to restrict the geometry of monomer coordination and polymer propagation. Therefore, the selection of electron donor compound is important for Z-N catalyst to cope with both the high stereo regularity and the high catalyst efficiency.

On the other hand, metallocene type catalyst has become commercially used for PP recently. The stereo regularity of metallocene-based PP is mostly determined by the ligand structure of the transition metal complex instead of the electron donor (Figure 2). The ligand with the proper molecular design not only gives the high stereo regularity control capability and the high catalyst efficiency but also provides the uniform copolymerization structure of product. Japan Polychem Corporation has commercialized the metallocene-based propylene-ethylene random copolymer (RCP) WINTEC® using its proprietary catalyst technology.[2] Conventional Z-N catalyst tends to provide the larger amount of extractable fraction along with the lowering crystallinity of RCP for the lower melting point. Contrarily, metallocene catalyst dramatically reduces the amount of extractable fraction even at the very low melting point, and WINTEC® mRCP is highly evaluated as the clean material suitable for the food packaging and the medical use (Figure 3, 4).

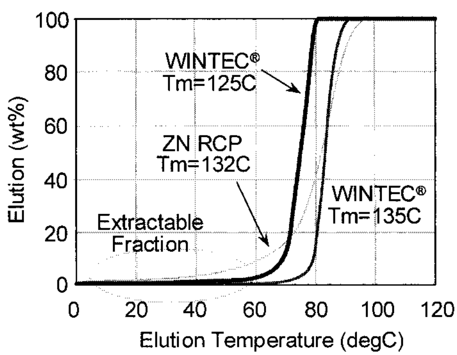



Fig. 3. Crystallinity distribution of PP random copolymers (RCP).

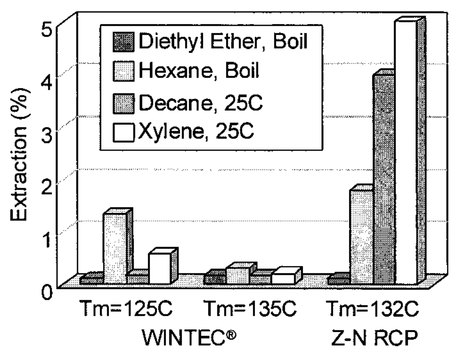



Fig. 4. Extractable fraction of RCP (WINTEC® is metallocene-based PP of Japan Polychem).

The crystalline morphology control is a commercial example of the higher order molecular structure control of PP. The size of spherulites in PP dominates scattering of light to lower the transparency, but the growth of spherulite can be controlled by addition of nucleation agent (Figure 5). This technology is driving the use of PP for the food-packaging sheet with the higher heat resistance compatible to the current A-PET and PS materials.

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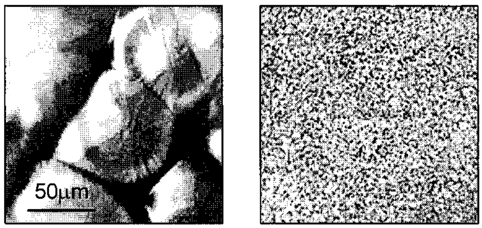


Fig. 5. TEM image of natural PP spherulite (left) and spherulite with phosphate salt nucleation agent (right).

Recent studies on metallocene-based PP have revealed several characteristic crystalline properties owing to its uniform molecular structure. Metallocene-based RCP, for example, shows high spherulite growth rate under the super-cooling condition, which results in the finely dispersed spherulite structure, and these are expected to provide the practical benefits.[3] On the other hand, PP block copolymer, or impact copolymer (ICP), which market is expanding around the automotive application, requires the precise molecular design and morphology control of rubber component. Metallocene catalyst technology is also expected to materialize the ideal molecular structure of ICP.

## PP Composite and Other Technologies

Automotive materials are the most highly functionalized and differentiated application field of plastics. The weight reduction of auto parts using PP meets the objectives of recent automobile improvements, such as the better mileage, $CO_2$ reduction, and so on. Besides, the good balance of mechanical properties, practical performances, and cost of PP is expanding its application (Figure 6).[4]

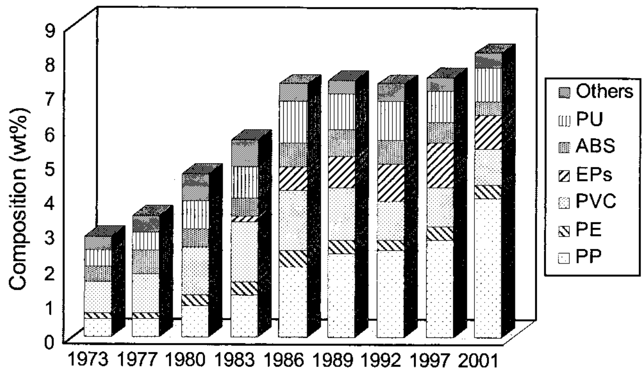


Fig. 6. Plastics materials and their composition used in Japan small cars (EPs=engineering plastics).

PP is widely used for various automotive parts, for example, large sized parts of bumpers and instrument panels, which require high safety and good appearance, other interior parts, and under-the-hood parts. The development of PP composite technology, which enabled the precise blend and distribution of rubber component and fillers, has expanded the viability of PP. PP composite meets the various parts design requirements owing to its wide range of blend composition and the versatility of compounding facilities with their size and functions. PP composite provides the mechanical properties compatible to engineering plastics and is replacing other materials taking advantage of its light weight and recycle suitability (Figure 7).

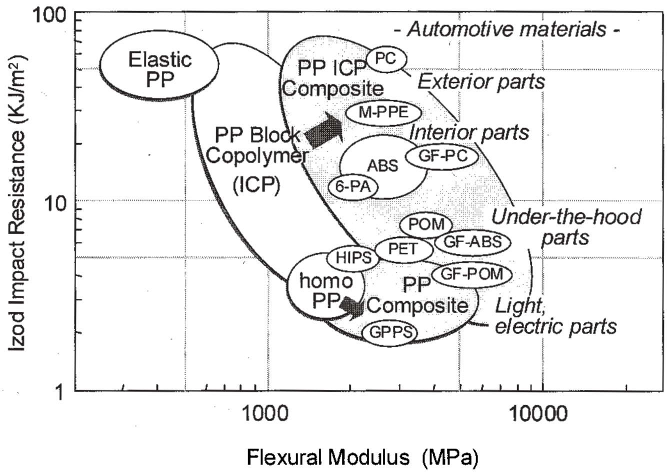


Fig. 7. Product range of PP composites for automotive applications.

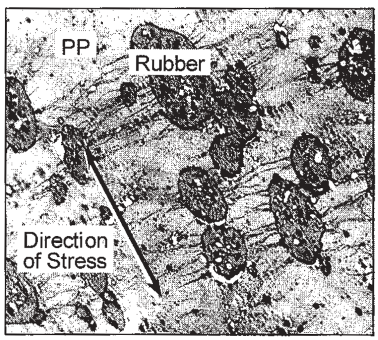


Fig. 8. TEM image of PP-rubber composite after impact absorption.

ICP is used directly or after compounding to form industrial parts. ICP is composed of homo PP and propylene-ethylene copolymer rubber components (Figure 8), which are commonly produced successively using cascade polymerization reactors. ICP should contain 30 to 40 percent of rubber to satisfy the high impact resistance required for the automotive exterior parts such as bumper. Z-N catalyst, however, has a limitation of the reactor-made rubber content due to the increased extractable fraction, which causes the operation difficulties and the inferior product performances. This makes the blend of additional rubber after polymerization necessary for ICP. There have been many efforts to optimize the manufacturing process, for example, molecule design improvement selecting polymerization catalyst and process and increased rubber content to reduce the additional rubber. Metallocene catalyst technology is expected to be suitable for this purpose.

Recently, the research for PP nano-composite (PPNC) is highlighted.[5] PPNC is composed of PP and finely dispersed filler such as clay, which commonly has the width or thickness of 1 nm scale and the length of more than 100 nm. PPNC is estimated to give the same stiffness of usual PP composite with c.a. 1/10 amount of filler and expected to contribute the weight reduction of auto parts. This high efficiency is assumed to be the combination of two factors, that is, the mechanical effect, which can be predicted from the filler aspect ratio, and the PP crystalline structure effect, which is induced by the finely dispersed filler (Figure 9, 10). Though PPNC is not widely commercialized yet due to the difficulties in the production technology, PPNC is expected to provide not only the mechanical strength but also other functions such as gas barrier and fire retardant capabilities.

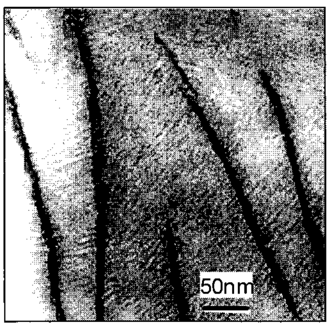


Fig. 9. TEM image of PP-clay nano-composite by melt extrusion method.

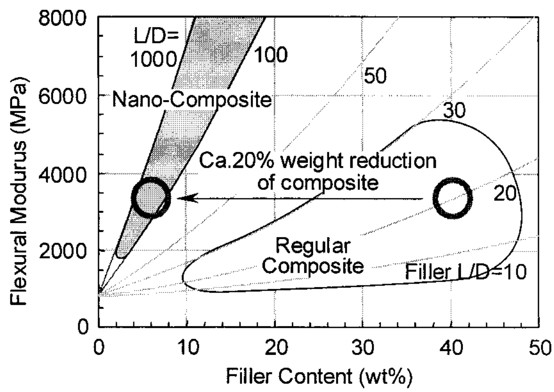


Fig. 10. Simulation results of filler aspect ratio effect on the filler content and stiffness correlation.

Foaming technology is rapidly spreading for the auto parts manufacturing in relation to the weight reduction, and PP foam has been used for impact absorption at the collision in the interior parts and bumpers. Recent molding technology is broadening the application of PP for the interior parts such as the door trims contributing to the further weight reduction. Foam material is required to be consistent with uniform bubble formation, which is enabled by the specific visco-elastic properties, or "strain hardening". Several methods have been developed and commercialized to control the visco-elastic properties of PP such as introduction of cross-linking or long chain branching. Besides the material technology, several new molding technologies have been developed, for example, the use of super critical fluid to control the melt flow and the combination of low pressure injection molding and expansion molding with the controlled mold opening ("Core back expansion").

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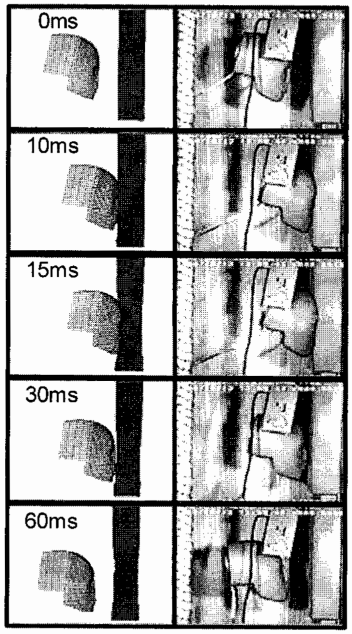


Fig. 11. Impact analysis for pillar design: results of simulation (left) and validation (dummy test: right).

As the polyolefin application spreads and the advanced material designs and new molding technologies are applied, the technologies of numeric simulation increase their significance.

Many kinds of software have been developed for computer-aided engineering (CAE), for example, flow analysis, mechanical analysis, impact analysis, and so on, and have become commonly used to optimize the parts design and processing conditions. Typical CAE applications are the calculation of polymer melt flow and pressure-temperature distribution in the mold during processing, the analysis of resin cooling process to predict the product qualities, and the estimation of mechanical properties of molded parts. It is important for the auto interior parts, such as pillar, to predict the potential damage to the human body in case of collision to secure the passengers' safety, and the simulation results are reflected in the parts design including the material properties (Figure 11).

## Conclusions

Despite the long history beyond fifty years since commercialized, polyolefin industry is still expected to be spreading its applications. The ceaseless effort to create highly designed materials is important to keep up with the changing market demands using the various technologies as discussed above. The latest technologies, such as metallocene catalyst, nano-composite, and numeric simulation, are expected to support that effort.

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