

Polypropylene Compounds for Automotive Applications

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Engineering plastics and metals have been extensively replaced by polypropylene (PP) based materials in automotive parts in order to achieve weight reductions and cost savings. To accomplish this, PP compounds which are made from PP and other components are under intense investigation. In this paper, we review the progress of research into compounding technology, improvement of mechanical properties and functionalization. Some problems and solutions for injection molding are also summarized. Furthermore, material developments for environmental load reduction are shown.

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Introduction

Because polypropylene (PP) is low in cost but has outstanding mechanical properties and moldability, it accounts for more than half of all the plastic materials used in automobiles. PP compounds are used for a variety of parts, including bumper facias, instrumental panels and door trims. Several grades of PP compounds, with their diverse performance characteristics, have been developed by compounding PP with various other materials according to the performance requirements of the intended parts. As of 2007, 3.75 million tons of PP (8% of the world's total PP consumption of 45.5 million tons) and 690,000 tons of PP (approximately 23% of the total domestic PP consumption of 2.94 million tons) are used for automotive applications.¹⁾ In recent years the environmental adaptability of PP has drawn significant atten-

tion. Therefore, it is expected that PP consumption will continue to increase in the future.

Fig. 1 shows an example of a general constitution of PP compounds for automotive applications. The impact strength of the “impact PP,” which is composed of homo PP and ethylene propylene copolymer (EP copolymer), is improved by adding an ethylene-based elastomer such as ethylene-butene or ethylene-octene copolymer, to which inorganic filler such as talcum is added for enhanced rigidity.

The growth of PP compounds for automotive applications has thus far been supported by the improved performance of PP resins—which serve as the base of PP compounds—and advancements in compound technology. With respect to the former, catalysts and the polymerization process have been continually, energetically improved in order to control the primary and higher-

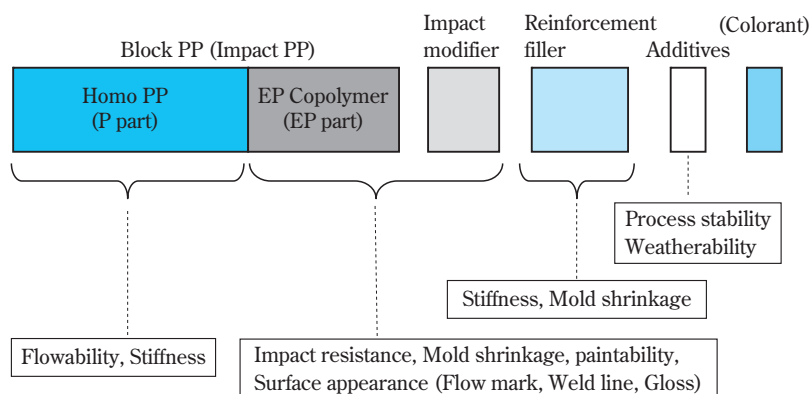


Fig. 1 Component of PP compound for automotive application

order structures of polymers. Regarding the latter, improvements in the performance and dispersibility of elastomers, as well as the control of particle size, dispersion and interface of inorganic fillers, have been attempted up to the present time.

Generally, the catalyst currently used for industrial purposes is the Mg-Ti type, otherwise known as the Ziegler-Natta (ZN) catalyst. Subsequent to the discovery of ZN catalyst in 1953 (and 1954), the improvement of its performance has been continuously attempted. In the course of such development the polymer activity, stereoregularity and morphology of polymer particles have been improved, thus contributing greatly to the simplification of the polymerization process as well as to the improvement of PP performance (Fig. 2). Since the beginning, the development of PP catalyst has been conducted with focus on two areas: polymer activity and stereoregularity. The standards of these properties are becoming extremely close to the ultimate. In recent years catalyst developments have been conducted with increased emphasis on control over molecular weight (distribution) and copolymerization reactivity.

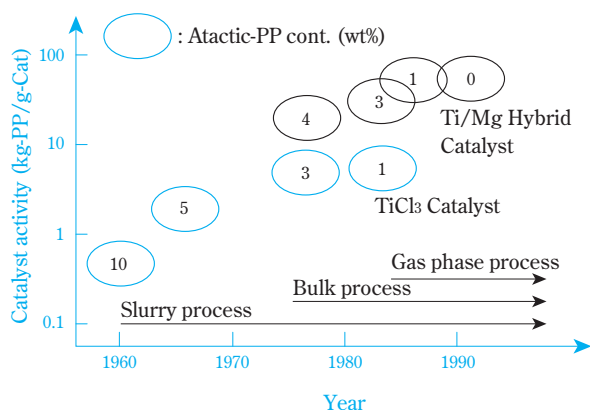


Fig. 2 Development history of Ziegler-Natta catalyst and polymerization process for PP

The PP manufacturing process, accompanied by improvements in the performance of ZN catalyst, has transitioned from the slurry polymerization method, which contains the residual catalyst removal process and the by-produced amorphous polymer removal process, through the bulk polymerization method, which utilizes liquefied propylene as a solvent, and then to the gas phase polymerization method, which doesn't use the amorphous polymer/residual catalyst removal system. This transition has propelled the streamlining of the PP manufacturing process while promoting energy conservation.

Currently, several unique process methods (such as a loop-type reactor method having two polymerization zones) are being developed in order to expand the molecular weight distribution and control the composition distribution of copolymers in an effort to achieve higher functionality and performance in PP.²⁾

With respect to resin-based automotive parts, lower weight is demanded for the sake of reduced environmental burden and better design and higher moldability are also required. In response to that demand, various phases of PP compounds for automotive applications have been improved. The improvements made thus far include greater rigidity, impact strength, fluidity and crystallization. Such enhancements of PP compounds have been achieved by compounding PP with additives such as elastomers and/or various inorganic fillers, as well as through higher stereoregularity, fluidity and rubberization which have been achieved with the aforementioned improvements in catalysts and the manufacturing process. Thanks to these improvements, a wide range of performance requirements in automotive parts, for which various engineering plastics were conventionally used, can now be covered by PP compounds alone (Fig. 3). As a result, PP-based material consumption in automotive applications has continued to increase. The details of the compound technology will be described in the following section.

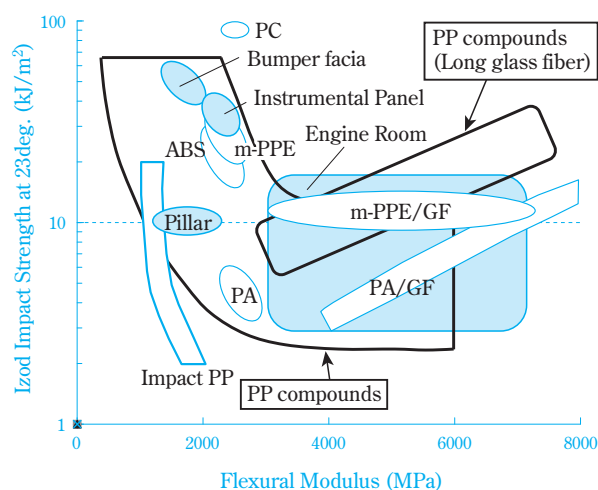


Fig. 3 Mechanical properties of PP compounds

Compound Technology

Twin-screw extruders are most commonly used for the production of PP compounds for automotive applications. It is essential that the twin-screw extruder has high pro-

ductivity as well as the ability to disperse the additives such as elastomers and fillers within PP and prevent the degradation of the material during the manufacturing process. In recent years, accompanied by increased applications in light-weight vehicles, materials having high fluidity (which facilitates thin-wall molding) have been in demand. Because this type of material has the low melt viscosity of PP, which is the main component, the design of the extruder's screws is important in order to adequately disperse the additives.

Table 1 History and development of extruder

Generation	Number of threads	Outer/Inner screw diameter (D_o/D_i)	Shaft torque ratio (Md/a^3) Nm/cm ²	Maximum screw speed rpm
1	3	1.22	3.7	150
2	2	1.44	5.0	300
3	2	1.55	8.7	600
4	2	1.55	11.3	1200
5	2	1.55	13.6	1200

Md: Torque, a: Shaft and axle distance

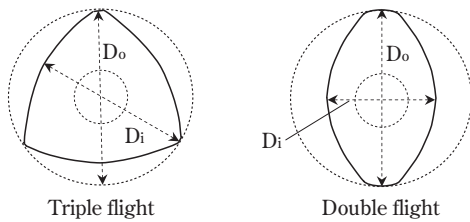


Table 1 shows the history and development of twin-screw extruders. The productivity and performance of twin-screw extruders can be characterized by the groove depth, the rotational speed of the screws and the motor's performance. It can be observed that the groove depth, rotation speed and torque have increased along with the generational progress.

As previously described, talcum is added to PP compounds to give them more rigidity. The use of talcum having finer particles has become the mainstream, accompanied by more demanding performance requirements. **Fig. 4** depicts the effect of talcum particle size on the discharge rate.³⁾ When using talcum at a minute particle size, the discharge rate significantly decreases at the same screw rotational speed. This is because when supplying the granulator with talcum having a minute particle size, the air between the particles is also brought into the machine, which causes the backflow of air toward the upper stream of the screws and results in the deterioration of material supply performance.

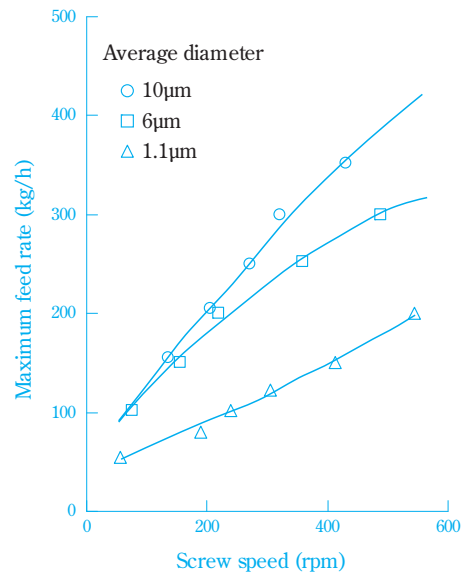


Fig. 4 Effect of talcum diameter on maximum feed rate

To address this issue, screws having the design shown in **Fig. 5** are used. In this design the screws maintain the resin in the semi-molten state in the primary mixing section, maintaining the space between the cylinder and the resin passing through the section, and then discharge the air that was brought in along with the talcum through a vent port located on the extruder's downstream side. Compared to the conventional extruder, which melts resin entirely within the primary mixing section, this system can significantly improve the productivity of the extruder by allowing the air to escape toward the downstream of the extruder.

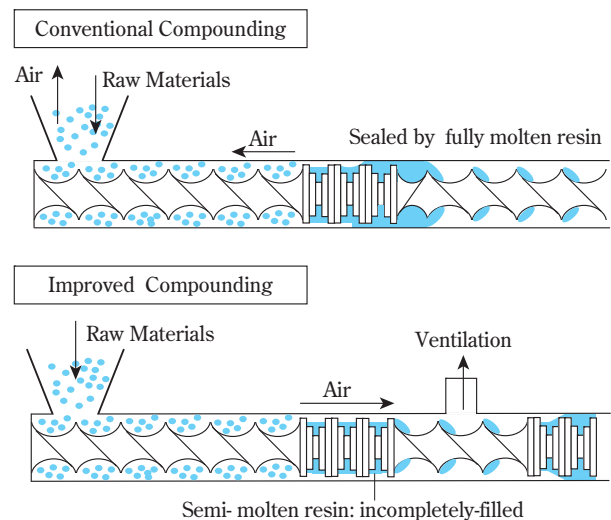


Fig. 5 Concept of screw pattern for high throughput compounding

Improving the Rigidity and Impact Strength of PP Compounds

Inorganic fillers are added in order to improve the performance of PP. **Table 2** shows the inorganic fillers used for property modification.⁴⁾ **Fig. 6** shows the stiffening effects of calcium carbonate in a granular state, tabular-shaped talcum and needle-shaped glass fiber. Of all these fillers, glass fiber—which has the high rigidity and aspect ratio—shows the greatest stiffening effect, followed by the tabular-shaped talcum. Given the considerations of cost, performance and processability, talcum and glass fiber are mostly used for PP compounds for automotive applications.

Table 2 Fillers for PP compounds

Inorganic Compound	Oxide	Silica, Titanium oxide, Magnesium oxide, Antimony oxide
	Hydroxide	Aluminum hydroxide, Magnesium hydroxide, Calcium hydroxide
	Carbonate	Calcium carbonate, Dolomite
	Sulfate	Basic magnesium sulfate
	Silicate	Talcum, Clay, Mica, Glass fiber, Glass balloon, Glass beads, Calcium silicate, Montmorillonite, Bentonite
	Carbon	Carbon black, Graphite, Carbon fiber
Organic Compound	Wood powder, Jute, Kenaf fiber, Hemp fiber, Nylon Fier, Aromatic polyamide fiber	

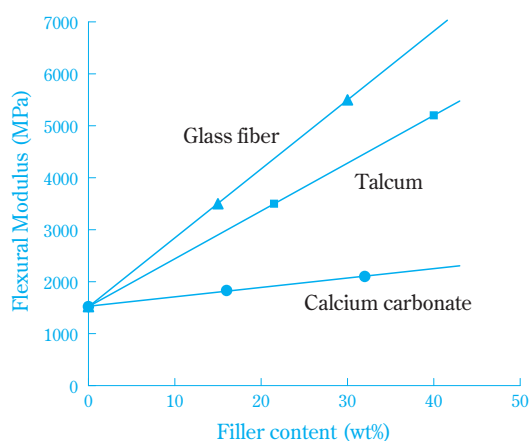


Fig. 6 Stiffening effect of fillers

Fig. 7 shows the effect of talcum particle size on the Izod impact strength. **Fig. 8** shows the effect of the talcum aspect ratio on the flexural modulus. It can be observed that the Izod impact strength increases as the talcum particle size decreases and that the rigidity improves as the talcum aspect ratio increases. Conse-

quently, it can be expected that greater rigidity can be achieved by further decreasing the particle size of the filler. For this reason a great deal of nanocomposite PP-based material development has been conducted.

Numerous studies have been implemented in regard to PP-based nanocomposites using montmorillonite as a filler. By optimizing the organification treatment agent used to cleave between two layers of montmorillonite, or by optimizing the constitution of the modified PP used to improve the dispersion of montmorillonite, PP compound with greater rigidity can be obtained.⁵⁾ However, virtually few PP-based nanocomposites have been put to practical use, because the melt viscosity increases as the area of resin/filler interface increases, the organification treatment agent is required for nano-dispersion of the filler, and the manufacturing process cost is high.

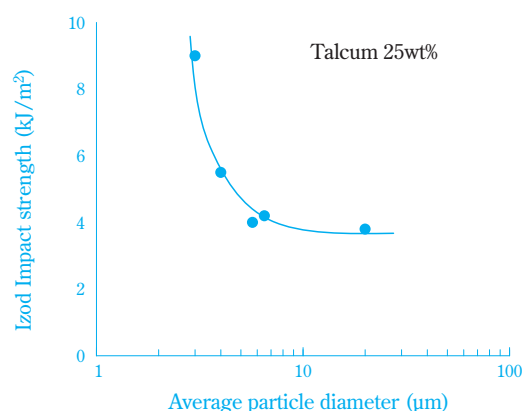


Fig. 7 Effect of talcum diameter on Izod impact strength

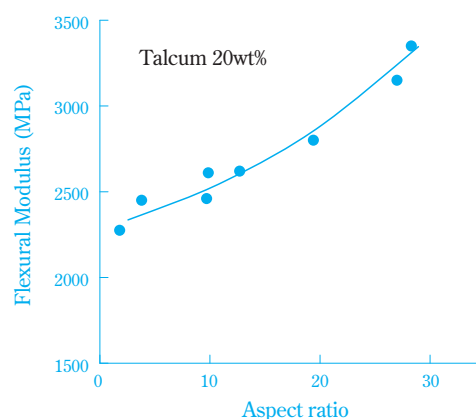


Fig. 8 Effect of aspect ratio of talcum on flexural modulus

Recently, the technology to selectively disperse filler to a specific phase has been developed. **Fig. 9** shows the effect of a modified elastomer obtained by adding calcium carbonate to PP/elastomer. While the calcium car-

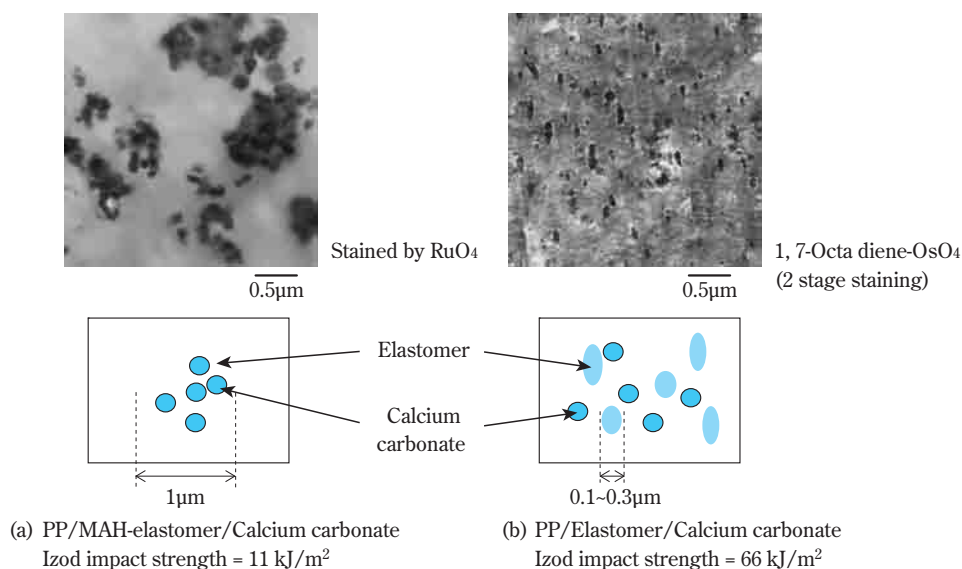


Fig. 9 Dispersion position control of calcium carbonate

bonate selectively exists in the elastomer domain when the modified elastomer is added, when the modified elastomer is not added, it selectively exists in the matrix, which is PP. The mechanical properties and other properties change in response to the filler's dispersion position. In this system the impact strength increases when the calcium carbonate is dispersed throughout the matrix.

To improve the rigidity of PP, material development has been conducted using short-length glass fiber. By adding short-length glass fiber to PP, the threshold of heat resistance increases to a point near the melting point of PP. This type of PP is therefore used in automotive parts for areas to be exposed to severe heat, such as the engine compartment. Furthermore, in order to add even more rigidity, long glass fiber reinforced PP is currently under development. As shown in **Fig. 3**, the long glass fiber reinforced PP demonstrates an extremely

high flexural modulus.⁶⁾ Through this system a material having extremely high tensile strength can be obtained by extending the residual fiber length.

The short glass fiber reinforced PP is produced using a standard type of twin-screw extruder. However, in order to prevent the glass fiber in the compound from breaking, the side-feed method is used, by which glass fiber is added to the molten resin from the side of the extruder. On the contrary, the long glass fiber reinforced PP is produced according to the following procedures: Glass fiber is continuously supplied from glass-fiber rolls, in a manner called roving, to the molten resin in the impregnating die. The glass fiber is then coated with the molten resin. Lastly, the fiber is cut into 5 – 40 mm length (**Fig. 10**).⁶⁾ Thus the pellet length and glass fiber length are equal in the long glass fiber reinforced PP. Using these pellets, automotive parts are produced through injection molding. However, if the glass fiber breaks dur-

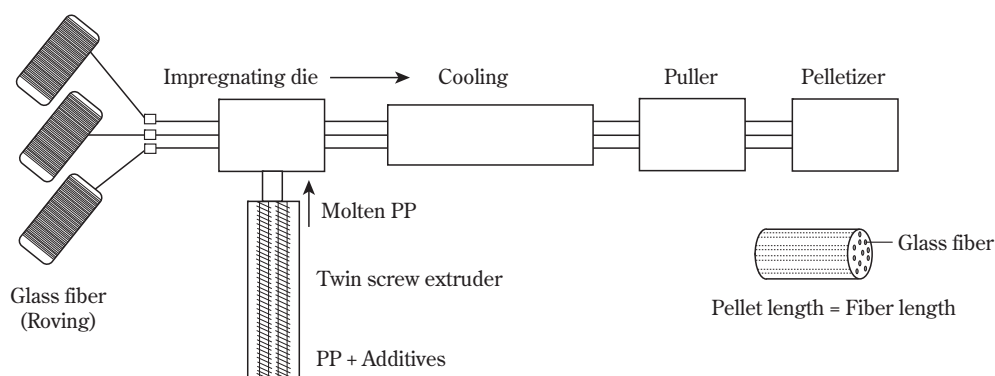


Fig. 10 Process for long glass fiber reinforced PP

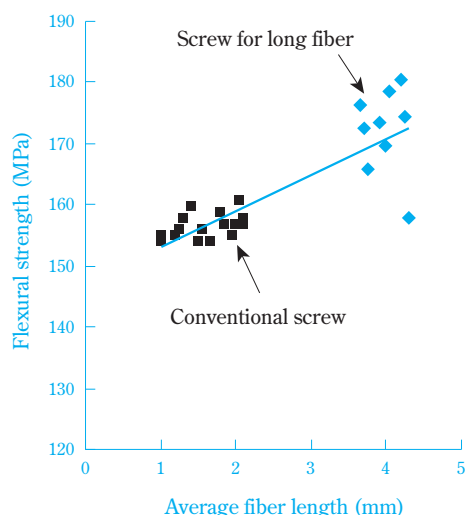


Fig. 11 Effect of screw type of injection molding machine on flexural strength

ing the injection-molding process, the rigidity of PP will deteriorate. Therefore, special screws having a minimal mixing effect are used (Fig. 11).

For example, the long-glass-fiber reinforced PP is used for front-end modules⁷⁾, back door panels⁸⁾ and door interior panels. In order to satisfy the performance requirements, it is important to have the technology that enhances the strength of interface between the glass fiber and PP. By optimizing the constitution of the modified PP to be used, the adhesive property of the interface between the PP and the glass fiber can be improved, thus manifesting excellent fatigue characteristics (Fig. 12).⁹⁾

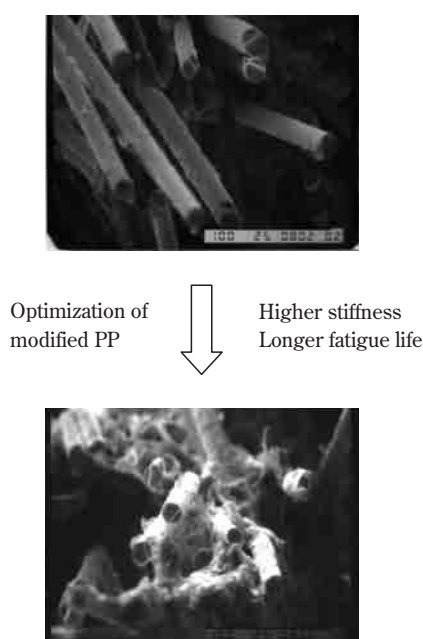


Fig. 12 SEM photograph of fracture surface of long glass fiber reinforced PP

Furthermore, because it is important to improve the dispersion of glass fiber for exterior parts, materials having excellent glass fiber dispersion suitable for this purpose are now being developed through an improved manufacturing method and the optimization of glass fiber.

Regarding other fiber-reinforced PP, carbon-fiber-reinforced PP and environmentally friendly organic fiber-reinforced PP are currently under development.

Improving Impact Resistance

The impact PP containing EP copolymer, as described previously, is used for PP compounds in automotive applications. Fig. 13 shows the ethylene content dependence of the EP rubber on glass-transition temperature. It is observed that the glass-transition temperature shows the minimum value when the ethylene content is approximately 60 wt%, and the performance as an impact modifier is good in this zone. However, the compatibility between EP copolymer and PP decreases as the ethylene content increases, and the dispersed particles increase in size. When the EP copolymer particle size becomes larger, impact resistance and tensile elongation deteriorate. For this reason EP copolymer with ethylene content of 30 – 40 wt% is often employed, considering a balance between the EP copolymer performance and the size of the dispersed particles. Thus it is desirable to minutely disperse EP copolymer particles having ethylene content of approximately 60 wt%. Therefore, it is hoped that the compatibilization technology will progress.

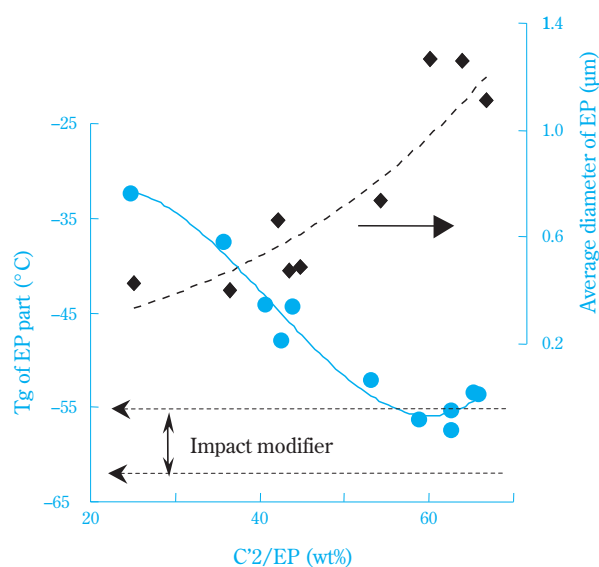


Fig. 13 Effect of ethylene content in EP copolymer on glass transition temperature and dispersion particle diameter of EP rubber

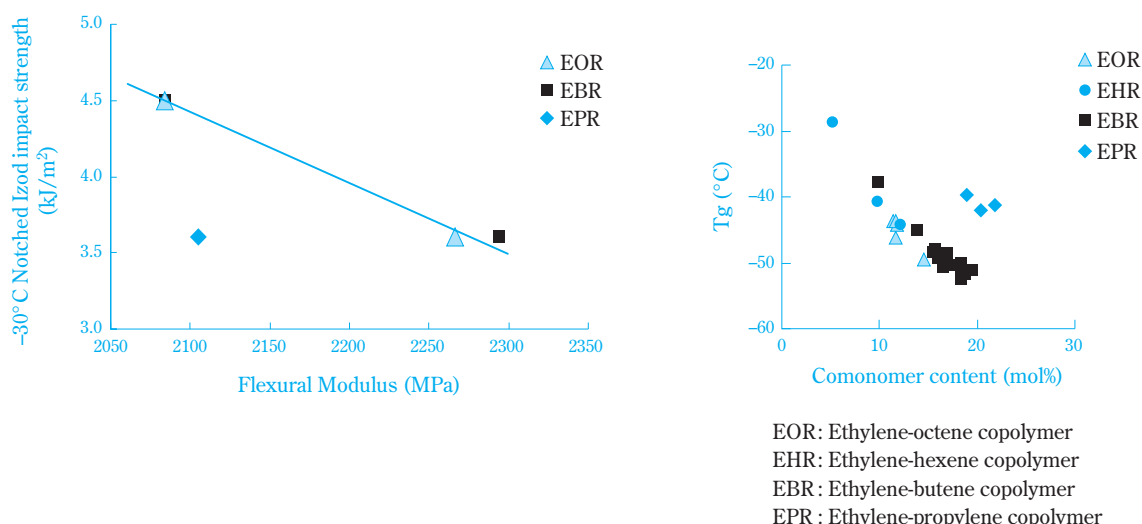


Fig. 14 Improvement of impact strength by addition of metallocene elastomer

Because EP copolymer is polymerized with a heterogeneous catalyst, the ethylene constituent distribution and molecular weight distribution between molecules are broad. Therefore, its performance as an elastomer is not satisfactory. For this reason a metallocene-based elastomer, e.g., ethylene-butene copolymer and ethylene-octene copolymer polymerized using a homogeneous catalyst, is often added as an impact-resistance modifier. Because the glass-transition temperature, compatibility with PP and melt viscosity of a metallocene-based elastomer change according to the co-monomer content and molecular weight, it is important to select a structure that will ensure a good property-modification effect (Fig. 14).

In recent years, accompanied by increased demand for light-weight automotive parts, there has been a rapid increase in the demand for PP compounds having higher fluidity. Although fluidity can be improved by decreasing the molecular weight of PP, which is used as the base, impact resistance decreases due to the decreased toughness of the PP resin and the enlarged dispersed elastomer particles. Therefore, styrene-ethylene butene-styrene (SEBS) tri-block copolymers are added to materials for which higher performance is specifically required. SEBS has a glass-transition temperature lower than that of ethylene-based elastomer. SEBS also causes the ethylene-based elastomer to disperse minutely. Thus its styrene content, butene content and molecular weight are precisely designed for this particular purpose. Fig. 15 shows the electron microgram of the SEBS-added material. SEBS is present at the interface between the PP and the ethylene-based elastomer, and the ethylene-based elastomer is minutely dispersed due to its compatibilization.¹⁰⁾

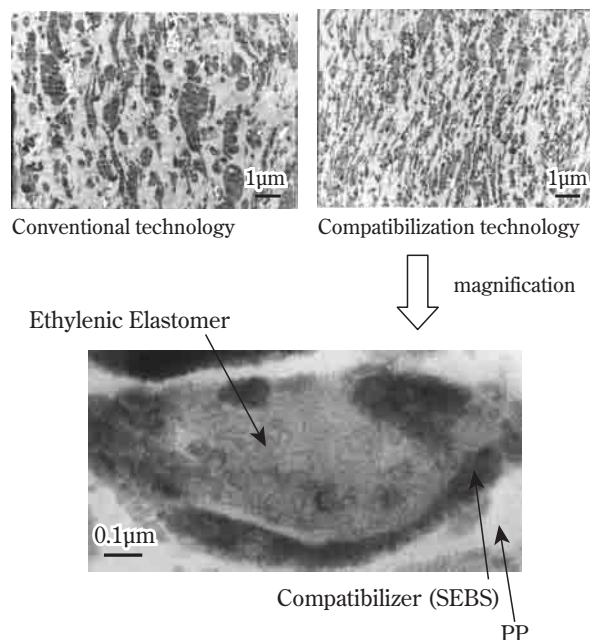


Fig. 15 Compatibilization of PP/ethylene elastomer with SEBS

Moldability of PP Compounds

Most of the PP compounds for automotive applications are made into automotive parts through injection molding. In this molding process the material is supplied to the cylinder of the injection-molding machine, melted at a temperature of approximately 200°C and injected into the die. However, various defects such as weld lines, flow marks, mold flashes, sink marks, warpage, thread formation and uneven coloring can occur during the molding process. Among such defect phenomena, the mechanisms of and solutions for flow marks, weld lines and mold flashes will be described in this paper.

Flow marks, which are among the molding-defect phenomena, resemble tiger stripes on the surface of the molded article. Consequently, flow marks are also called tiger marks. The mechanism for the generation of flow marks has been studied in considerable depth. As a result of such studies it has been found that flow marks are caused by unstable flow at the flow front of the molten resin.¹¹⁾ The flow stability of the flow front depends on the rheological property of the molten resin. **Fig. 16** depicts the effect of the swell ratio, which indicates the elasticity of the molten resin, on the flow mark phenomenon. The swell ratio is measured using a capillary rheometer, and defined in **Fig. 16**. The higher the swell ratio is, the stronger the elasticity of the molten resin will be. As the swell ratio increases, the length and occurrence of the flow marks will decrease. We believe this is because the flow stability of the flow front increases due to the increased swell ratio. **Fig. 17** shows the correlation between the swell ratio and the intrinsic viscosity (IVep) of EP copolymer contained in PP. The dependence of swell ratio on the intrinsic viscosity of EP copolymer depends on the ethylene content of EP copolymer (C2'inEP). When the ethylene content in EP copolymer is low, the swell ratio increases as the intrinsic viscosity increases. This means it is possible to reduce flow marks by optimizing the structure of the EP copolymer.

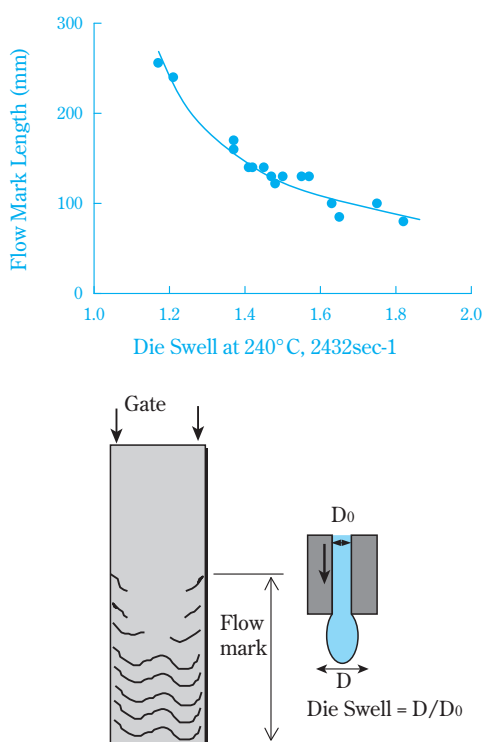


Fig. 16 Effect of die swell on flow mark length

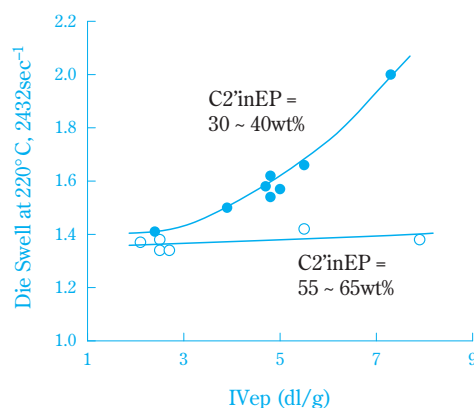


Fig. 17 Effect of EP copolymer intrinsic viscosity on die swell

The mechanism for the generation of weld lines, and solutions for it, will be described next. Weld lines demonstrate a stripe pattern that appears on the merging section of molten resin. Yokoi, et al. explains the mechanism for the generation of weld lines by focusing on the manner in which the extra surface area is taken up at the merging section. In order to do so, the weld-line formation process is first observed using a see-through die. The weld lines are then organized according to the merging angle (meeting angle) of the molten resin.¹²⁾ **Fig. 18** shows the SEM photograph of the weld-line section. It can be observed that the talcum and elastomer are significantly oriented in the area near the surface. Although a smooth surface is formed immediately after the die has been filled with molten resin, because the talcum and elastomer are oriented toward the direction of surface thickness in the resin merging section, the coefficient of linear thermal expansion becomes smaller than that of the general section, thus making the dimensional change small at the time of solidification and consequently form-

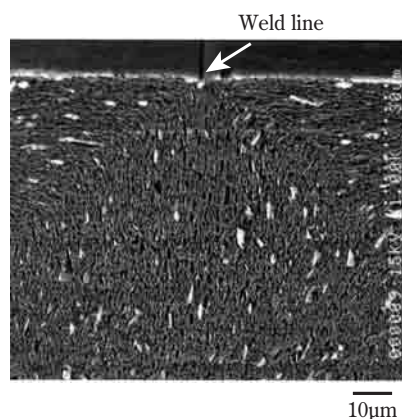


Fig. 18 SEM photograph of weld line section (Elastomer phase was extracted by Xylene)

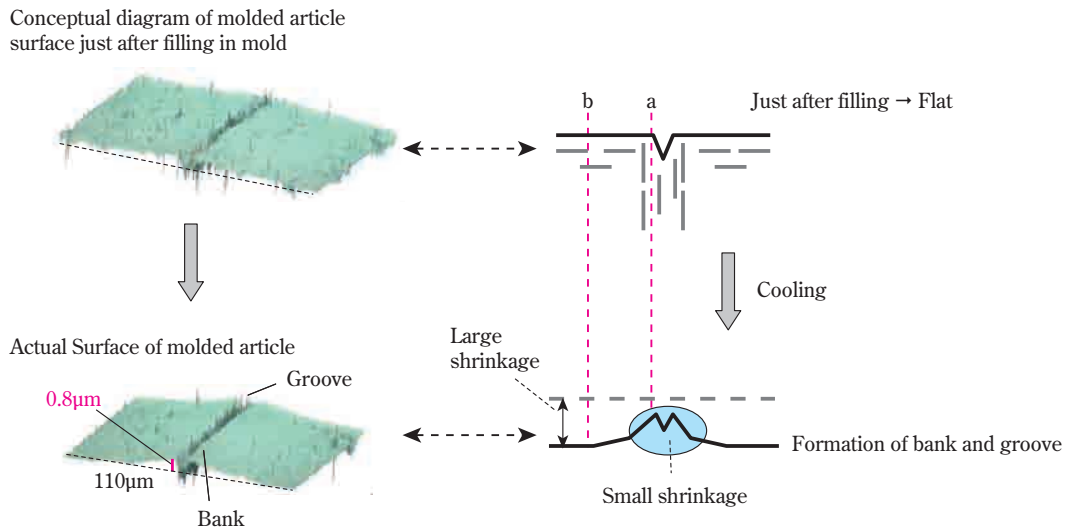


Fig. 19 Weld line forming process

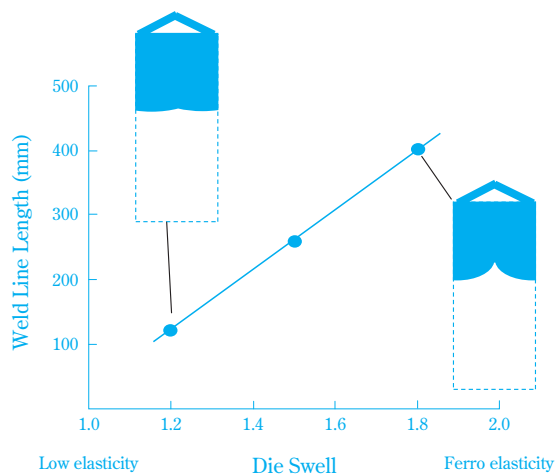


Fig. 20 Effect of die swell on weld line length

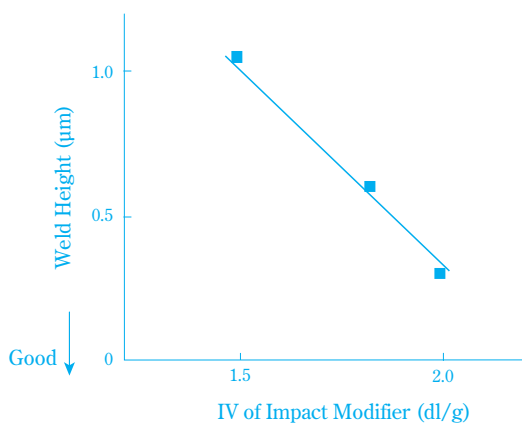


Fig. 21 Effect of intrinsic viscosity of impact modifier on weld height

ing a swelling shape (Fig. 19). As with flow marks, the rheology characteristics greatly affect the occurrence frequency of parallel weld lines on the merging section of the resin flowing in the same direction. Fig. 20 shows the effect of the swell ratio on the weld-line length. Contrary to the case of flow marks, the smaller the swell ratio is, the shorter the weld-line length will be.

Thus, although flow marks become improved when the swell ratio is higher, the weld lines become more visible and therefore worse. This means there is a trade-off relationship between these two phenomena. To overcome that relationship, there is a method of controlling the orientation of the elastomer, which is the orienting component. The elastomer, which becomes oriented in weld lines, is mainly added rubber having a low molecular weight. Fig. 21 depicts the relationship between the intrinsic viscosity of the added elastomer and the height of the weld-line swell. Even though the intrinsic viscosity is changed, the weld-line length does not change. However, as the intrinsic viscosity of the added elastomer increases, the swell height decreases, i.e., the swell becomes less noticeable. This is because of the fact that since the orientation is suppressed in the weld section if the added elastomer has high intrinsic viscosity, the difference between the coefficient of linear thermal expansion in the weld section and that in the non-weld section becomes smaller.

Pressure in injection molding occurs as the molten resin is being injected into the die. The resin pressure during the injection process is also greatly affected by the rheological characteristics of the molten resin. When the resin pressure is high, the resin enters the space between the dies, causing a defect phenomenon called

“mold flashes.” Fig. 22 shows the effect of swell ratio on the maximum resin pressure at the gate and that at the terminal during injection molding. The maximum resin pressure in a material having a large swell ratio is small at both the gate and terminal sections. By optimizing the EP copolymer structure design so that a high swell ratio can be obtained, a material that can be formed through injection molding at a low pressure, and that does not readily produce mold flashes, can be obtained.

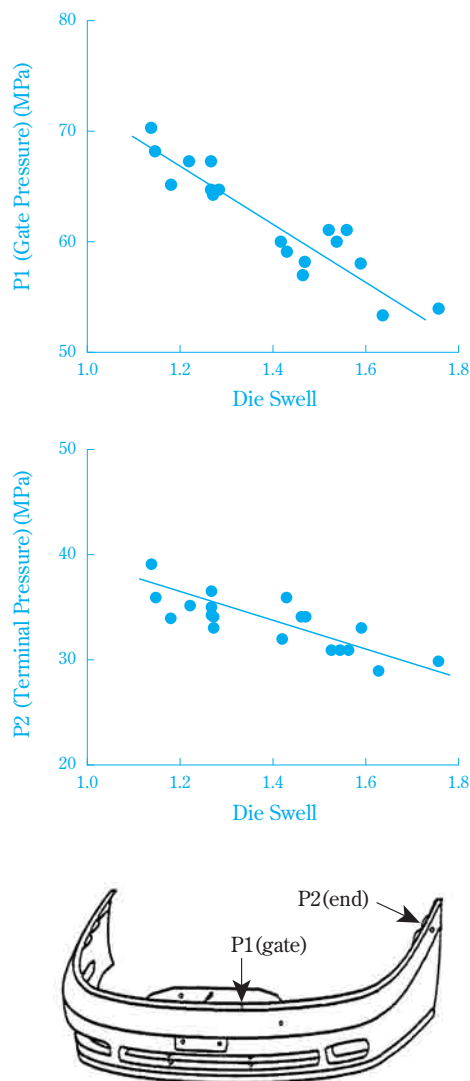


Fig. 22 Effect of die swell on resin pressure at gate and end position

Adding More Functionality

Conventionally, high rigidity, impact resistance and moldability have been demanded in PP compounds for automotive applications. In recent years, however, even more functions such as easy paintability, conductivity,

scratch-resistant property and low coefficient of linear thermal expansion are in demand.

Automotive parts such as bumper facias and side mouldings are often painted prior to installation. However, because PP resin, has poor adhesive properties, so the corresponding parts are painted after being primed with primer whose main constituent is chlorinated PP. In order to simplify the paint process, it is desirable to develop a PP-based material that can be painted without priming. In order to accommodate this need, the addition of a polyolefin incorporating a polar group to the material has been attempted. Fig. 23 shows the effect of OH content on paint adhesion.¹³⁾ We have studied the additions of several types of PP, each having a different OH content. The paint adhesion can be organized by OH content in the material. Primerless paint can be achieved by introducing approximately 1 wt% or greater of OH. However, it is currently difficult to obtain PP having both high molecular weight and high OH content. Therefore, in order to achieve primerless paint it is necessary to add a large amount of PP having a low molecular weight and containing a small amount of hydroxyl radicals, but such addition causes the PP's basic performance characteristics (e.g., rigidity and impact strength) to deteriorate significantly. Consequently, such a PP-based material has not yet been put to practical use.

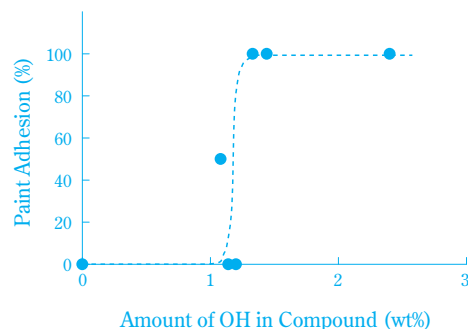


Fig. 23 Effect of OH content in PP compound on Paint adhesion

To achieve weight reductions in automobiles, resin applications for outer panels such as fenders and doors are currently being investigated. Thus far, polyphenylene ether/polyamide alloy and polycarbonate/ABS alloy outer panels have been put to practical use. When using a resin for outer panels, it is necessary to use the same paint as used on the surrounding metal parts in order to maintain the same color tone. Metal parts are painted through the electrostatic spray-painting method, which

takes advantage of the conductivity of metal parts. Because resin parts do not have any conductivity, primer having the conductivity is usually painted prior to the paint application. Subsequently, these resin parts are installed on the vehicle then painted together with the metal parts using the electrostatic spray-painting method. To reduce the number of procedures in the paint process, the addition of conductivity to PP compounds has been attempted. There is a method in which conductive carbon is added to resin materials in order to achieve that purpose. The particle size of conductive carbon is small, and such carbon has poor compatibility with PP. Therefore, when a large amount of conductive carbon is added to PP, the fluidity, impact resistance and elongation will decrease. Consequently, the amount of conductive carbon to be added must be minimized. To fulfill this requirement, the following method has been developed: High-density polyethylene (HDPE) is

blended as a disperse phase then the conductive carbon is placed in this phase to create a mesh-like dispersion state. While the electrical resistance is $10^7 \Omega/\text{cm}$ or greater in the system to which 3 vol% of carbon black has been added without HDPE, the other system to which HDPE has been added shows a low electrical resistance of $10^3 \Omega/\text{cm}$. This means the amount of conductive carbon needed to add conductivity to the PP-based material can be reduced by adding HDPE.¹⁴⁾

Regarding automotive interior parts, PP compounds are used for instrumental panels, door panels and pillars. Because these parts require the property of scratch-resistance, a coating is generally applied. However, a material having even more scratch-resistant property is currently being developed in order to reduce of the coating process. H. -J. Sue et al. have developed a load-variable type of anti-scratch testing method. The method has been adopted as the ASTM D2027-05.¹⁵⁾ Fig. 24 shows

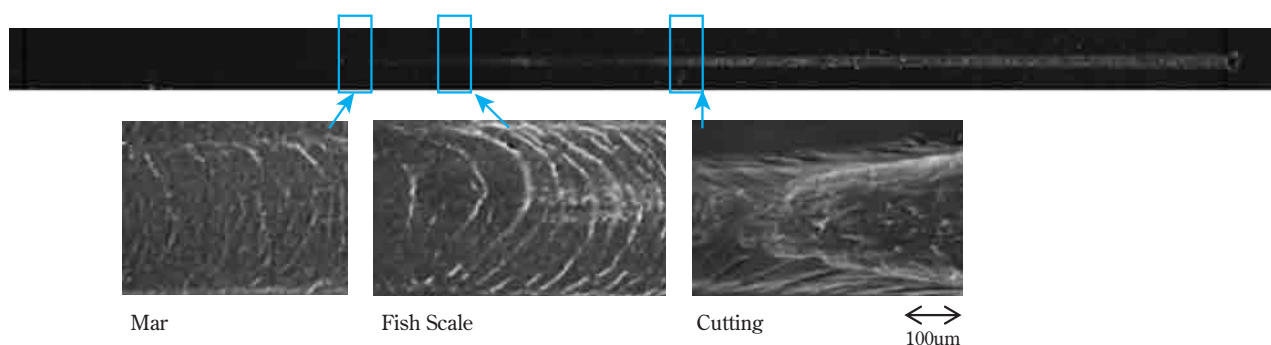


Fig. 24 Evaluation of anti scratch performance of PP/Elastomer/Talcum (ASTM D7027-05)

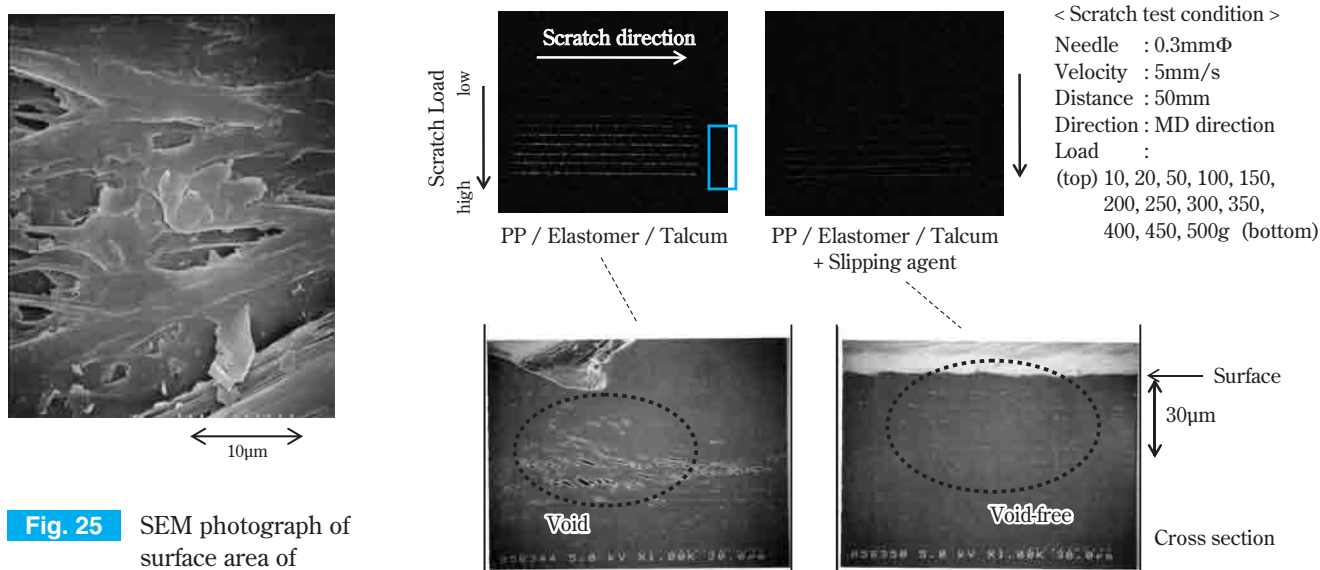


Fig. 25 SEM photograph of surface area of PP/Elastomer/Talcum after scratching

Fig. 26 Effect of slipping agent on anti scratch performance

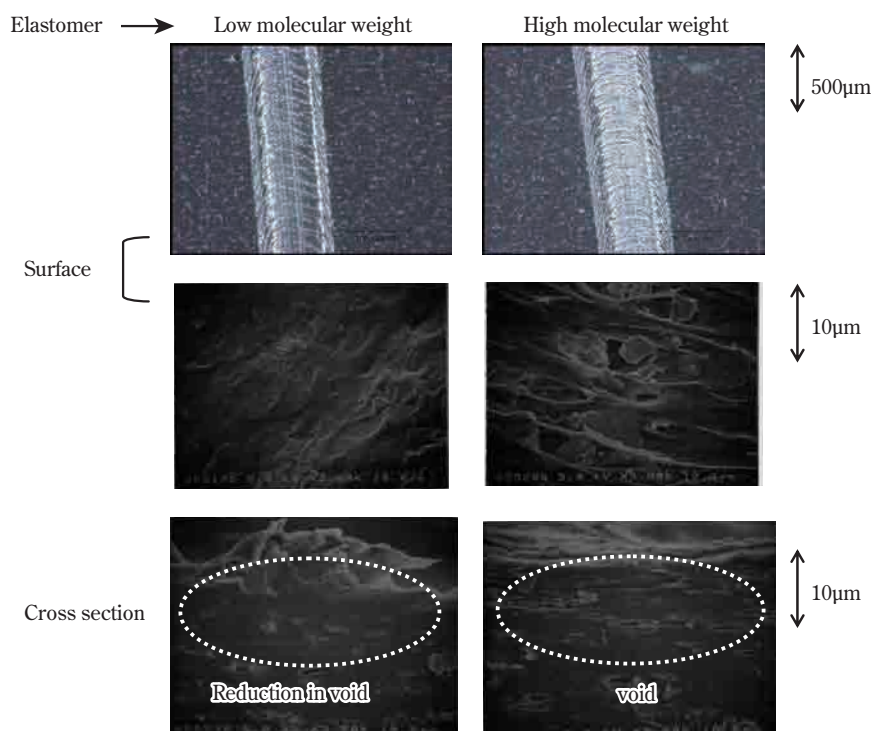


Fig. 27 Effect of molecular weight of elastomer on anti scratch performance

the anti-scratch performance of PP-based interior materials measured using this system. As the load increases, the mode of scratching changes in the following order: Mar → Fish Scale → Cutting. Observing the surface of the sample after the scratch testing, it is clear that PP is extended and the talcum is exposed (Fig. 25). Consequently, the scratched area appears to be white. The methods by which to improve the scratch-resistant property of PP include applying the lubricating property to the surface, increasing the material's yield strength, and improving the interface strength between the PP and the talcum. Fatty amide shows an excellent effect as a lubricant. Adding 0.2 wt% of fatty amide reduces the dynamic friction coefficient from 0.8 to 0.15. Fig. 26 shows the result of the anti-scratch performance test on PP containing fatty amide. The anti-scratch performance has been improved tremendously, due to the addition of fatty amide. In addition to the aforementioned methods, we have developed the method by which to improve the anti-scratch performance by controlling the morphology of the elastomer contained in the material. Fig. 27 shows the results of anti-scratch performance among the samples, each of which had a different elastomer molecular weight. In that figure the sample having a low molecular weight demonstrates better anti-scratch performance. The elastomer having a low molecular weight is more oriented toward the flow direction than the elastomer

having a high molecular weight, thereby reducing the occurrence of voids.

Environmental Responding Technology

1. Weight Reduction Technology Using Foam Formation

The foam molding technique accommodates the need for weight reduction. Conventionally, the injection-foam molding technique using a thermolysis chemical foaming agent has been put to practical use. By melting and injecting the blend of PP resin and thermolysis chemical foaming agent using an injection-molding machine, foaming parts having high expansion ratios of up to two times the original volume can be obtained. These foaming parts are used for door trim and other, similar parts. The foaming property of a material depends on the melt viscoelasticity and crystallization behavior of the resin. A material having the large swell ratio, which is the melt tension index, has air bubbles with high morphological stability, thereby forming a dense cell shape. Such material can be achieved using a cross-linked PP and PP having ultra-giant molecular weight (Fig. 28).

In recent years great attention has been given to a technology suitable for foaming parts having expansion ratios of at least two times the original volume, which is called the supercritical injection-foam molding

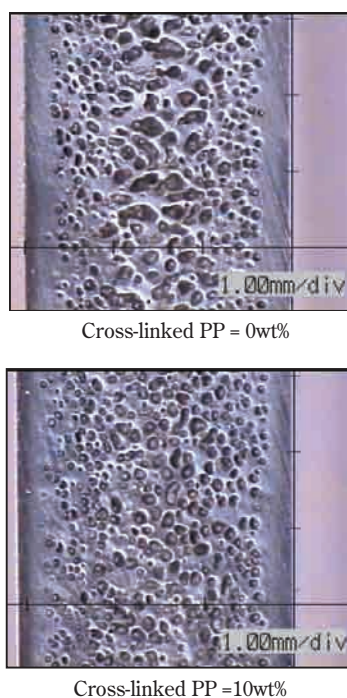


Fig. 28 Effect of cross-linked PP on cell shape of PP foam articles

method. A feature of this method is that foam-molded articles can be obtained via the following procedures: Carbon dioxide or nitrogen in the supercritical state is injected into the molten resin in the injection cylinder as a foaming agent. After allowing it to be absorbed into (and dispersed throughout) the molten resin, the resin is then injected into a die. Compared to the articles molded through the injection-foam molding using a chemical foaming agent, in this method the meltability of the blowing gas that is put into the molten resin can be increased and thus achieve a high expansion ratio. The use of a PP-based material suitable for this molding method enables us to achieve the molded articles having excellent appearance and cell shape, even with a high expansion ratio of at least three times the original volume (Fig. 29).

2. Compound Technology with Biomass-Derived Resin

To address the serious environmental issues represented by shortages of fossil resources such as petroleum due to the large consumption of such fuels, and of global warming due to the increased carbon dioxide concentration in the atmosphere caused by the combustion of fossil fuels, are now our pressing needs. Under these circumstances the development of biomass-derived resin has also been energetically conducted in the area of resin materials. Because photosynthetic plants are the basis of the raw material for biomass-derived resin, biomass-derived resin is essentially carbon neutral. Therefore, replacing the petroleum resin with biomass-derived resin can dramatically reduce the discharge of carbon dioxide. Polylactic acid (PLA) was the first biomass-derived resin to be put to commercial use, and its mass production is now advancing. From the perspective of environmental response it is desirable to use PLA for structural parts in the area of automobile manufacturing as well. In reality, however, the areas of PLA application have been extremely limited due to the following practical issues: poor impact resistance, poor durability, susceptibility to hydrolyzation, slow crystallization kinetic, and long solidification time during the injection-molding process. Therefore, the PP/PLA alloy material has been developed as a material that can be applied to a wide range of automotive parts. In the PP/PLA alloy material the essential shortcomings of PLA—poor hydrolyzation and moldability—have been overcome by designing the structure in such a manner that the PLA is surrounded by PP. Because the compatibility between PP and PLA is extremely poor, when simply blended the PLA will disperse unevenly with a large particle size over 10 μ m, thereby causing the impact resistance and moldability (appearance) to deteriorate significantly. Therefore, PLA's particle size is reduced through the reactive processing that utilizes a reactive compatibilizer (Fig. 30).¹⁶⁾

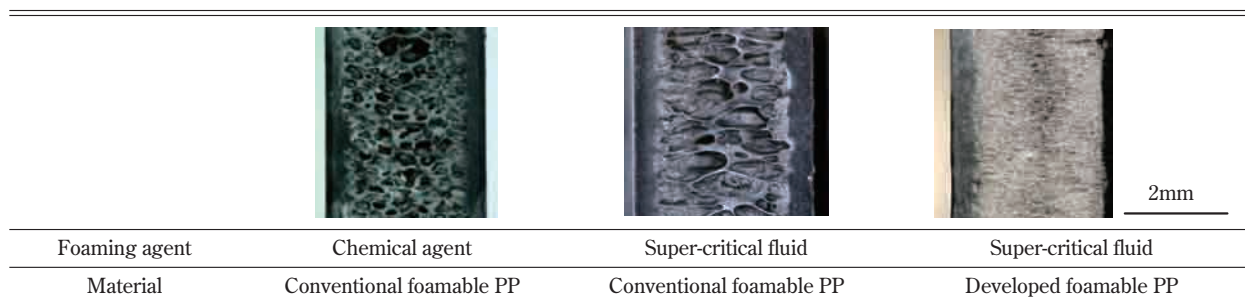


Fig. 29 Cross-section photograph of injection molded foam articles

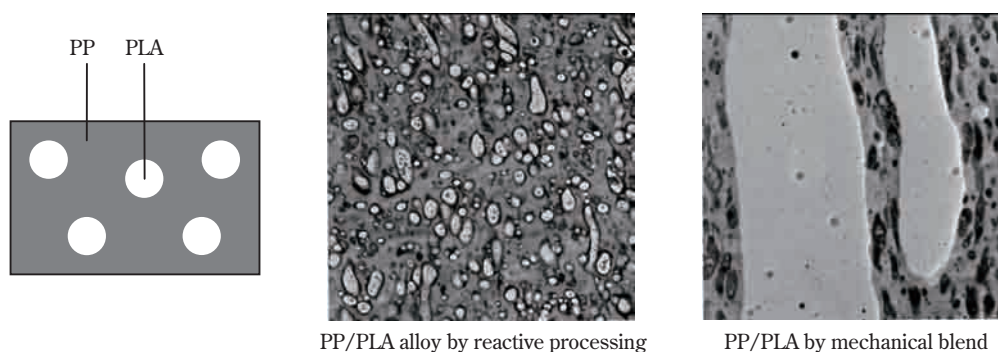


Fig. 30 Reactive processing of PP/PLA by using of reactive compatibilizer (TEM photograph: Stained by RuO₄, White domains are PLA)

Table 3 Mechanical properties and injection moldability of PP/PLA alloy

	Flexural modulus MPa	Izod impact strength ^{*1)} kJ/m ²	Moldability	
			Surface peeling	Mold temp./ Cooling time ^{*2)}
PP/PLA alloy (Fine dispersion of PLA)	1000	18	Good	30° C/30 sec.
PP/PLA Blend (Coarse dispersion of PLA)	1300	5	Poor	30° C/30sec.
PLA	4000	3	Good	30° C/120sec.
PP for interior parts	1100	18	Good	30° C/30sec.

*1) Measured at 23° C, *2) Mold releasable condition without deformation of article

Table 3 indicates the physical properties and moldability of a PP/PLA alloy material. The impact resistance and injection-molding moldability have been improved by alloying the material using a reactive compatibilizer. Furthermore, it demonstrates that the injection molding can be performed under the same conditions as with the regular PP.

Fig. 31 depicts the comparison between the resistance to heat and humidity of the PP/PLA alloy material and PLA material. While the physical properties of the mate-

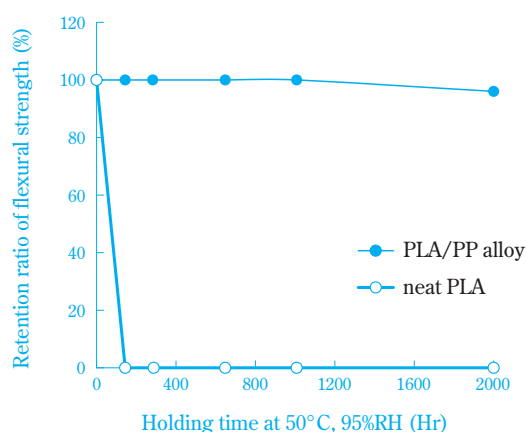


Fig. 31 Resistance to heat and humidity of PP/PLA alloy and PLA

rial containing PLA alone deteriorate within an extremely short period of time (approximately 100 hours), the alloy material satisfies the heat-resistance requirement for automotive parts.

Fig. 32 shows the result of LCA calculation pertaining to carbon dioxide. Compared to the existing PP-based parts, the abundance of carbon dioxide is reduced by approximately 10% in the alloy material.

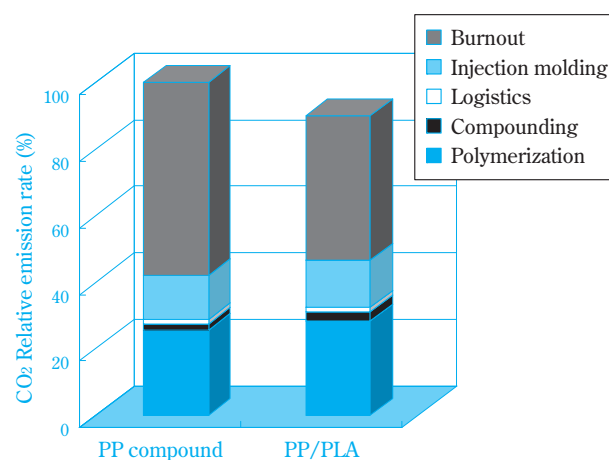


Fig. 32 Comparison of CO₂ emission between PP compound and PP/PLA alloy (Self-calculated data, CO₂ emission of PP compound equals to 100%)

Conclusion

It can be expected that, from this point forward, PP compounds will continue to play the primary role in resin materials for automotive applications due to their high cost-performance, outstanding moldability and environmental suitability. The application areas of PP compounds have expanded up to the present time due to improvements in the base PP as well as the advanced compound technology and molding technology. These technological developments have been supported by various theories and principles found through the techniques of structural analysis. We believe it is possible to expand the area of application for PP compounds by continuously developing these technologies. Regarding the base PP, precise control over the molecular weight distribution, the optimization of the EP copolymer structure and the technology of compatibilization are important factors. Therefore, advancement of both the catalyst technology and polymerization process technology is expected. For the compound technology it is hoped that the performance of elastomers and fillers, as well as the dispersion-control technology for compounds, will improve. In the existing injection-molding process a material is melted and poured into a die, wherein it solidifies by cooling. In injection molded PP parts the crystal structure and the structure of dispersion components (such as elastomers) incline toward the depthwise direction. By radiating light having a high brightness, their three-dimensional structures have gradually become revealed. We believe that managing these structures by molding and designing the material to be more controllable through molding will allow us to achieve performance characteristics that could not be obtained by the conventional PP compounds.

References

- 1) "Townsend Polypropylene Report 2008", Townsend, Chapter 2.
- 2) G. Mei, P. Herben, C. Cagnani, and A. Mazzucco, *Macromol. Symp.*, **245-246**, 677 (2006).
- 3) "Polymer ABC Handbook", SPSJ, Koubunsi ABC kenkyu-kai Ed., NTS Inc.(2001), p.603.
- 4) H. Yui, "Polymer Based Composite materials", *Plastics Age* (2005), p.24.
- 5) E. Manias, A. Touny, L. Wu, K. Strawhecker, B. Lu, and T. C. Chung, *Chem. Mater.*, **13**, 3516 (2001).
- 6) H. Suzuki, Seikei-Kakou, **20** (6), 343 (2008).
- 7) M. Atsumi, I. Inai, A. Sasano, K. Kitano, 2006 JSAE Annual Congress (Spring), 17 (2006).
- 8) T. Iwata, T. Iriguchi, K. Watanabe, S. Suzuki, Hitachi Chemical Technical Report, **44** (1), 21 (2005).
- 9) K. Kitano, K. Atarashi, M. Tsuji, 15th JSPP Annual Meeting, 27 (2004).
- 10) K. Ookawa, S. Susumu, T. Watanabe, *Polyfile*, **42** (5), 71 (2005).
- 11) H. Yokoi, K. Yokoi, Seikei-Kakou, **20** (10), 737 (2008).
- 12) H. Yokoi, Y. Murata, K. Oka, K. Watanabe, Seikei-Kakou, **9** (4), 290 (1997).
- 13) Mitsui Chemical Co. Ltd., Toyota Motor Co., Sumitomo Chemical Co. Ltd., Jpn Kokai Tokkyo Koho 2005-264033.
- 14) H. Yui, G. Wu, H. Sano, M. Sumita, and K. Kino, *Polymer*, **47**, 3599 (2006).
- 15) E. Lau, G. T. Lim, M. Wong, B. Browning, A. Moyse, and H. -J. Sue, "Automotive Thermoplastic Polyolefins(TPO) Global Conference 2005", Society of Plastics Engineers (2006), p.296.
- 16) S. Moritomi, *Polyfile*, **46** (1), 40 (2009).

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