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ADVANCED PE100 GRADE WITH AN EXCELLENT BALANCE BETWEEN DURABILITY AND PROCESSABILITY

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ABSTRACT

Polyethylene has been used for various pipe applications. In particular the use of PE100 material has been expanding in pressure pipes for gas and water service. In general, PE100 materials have very high molecular weight component in order to improve the performance of durability, so they have high viscosity and their processability are usually poor. Responding to increased demand of PE100 pipes in the market, requirements for the improved production efficiency are growing. To meet those customer needs, we developed a new PE100 grade which has an excellent balance between durability and processability. In PPXIII, we have reported PE100 grade (NOVATEC™ HD HE212W, HLMFR=9g/10min) which has extraordinary resistance to slow crack growth (SCG) ; notch pipe test (NPT) >20,000h, using our Advanced Multi-modal Slurry Loop Process (AMSLP), which has 3 cascade reactors, and a high performance catalyst. As a result of further refining on this technology, we have succeeded in developing a new PE100 grade (NOVATEC™ HD HE222W) which has the best balance between flowability and SCG resistance. The new PE100 grade whose HLMFR is 18g/10min shows excellent processability, for example, >10% less extrusion load, >20% less injection pressure and better surface finish of injection molded fittings than a conventional one. Moreover, it is possible to mold at lower temperature. Lower processing temperature decreases the risk of processing defects such as burn particles and die drool, it also contributes to energy saving. These features are expected to drastically improve production efficiency of both pipe extrusion and fitting injection. Regarding the durability of the new PE100 grade, it keeps very good SCG resistance level. NPT result of >5,000h determined at our laboratory is far more superior to the specification in ISO 4427 and ISO 4437. We believe that our new PE100 grade can contribute to the further growth of plastic pipe industry.

INTRODUCTION

Advantages of polyethylene pipe

Polyethylene (PE) has already established and is expanding its position as a major material for many pipe applications based on its excellent characteristics such as light weight and flexibility for easy handling and its superior chemical stability. The flexibility of PE pipe gives it a great ability to follow the ground movement. Even in the Great East Japan Earthquake (magnitude 9.0) that occurred on March 11, 2011, no damage of PE pipe system (for water supply) was reported in spite of its terrible shock.[1] Excellent strength of PE pipe system to the earthquake is now widely acknowledged in Japan, and PE pipe system is governmentally recommended as one of the earthquake-resistant pipe systems.

Globally, PE100 market is rapidly expanding based on its reliability for gas and water delivery services, together with the spreading of larger diameter pipes and reduced cost installation technologies such as no-dig and no-sand method, which is realized by the successful development of PE100 materials with superior SCG resistance.

Recent needs for PE100 material

With the growing concerns for environmental issues such as global warming caused by Green House Gas emissions and natural resources depletion, suitable measures to reduce such environmental impacts are strongly required these days. In that context, needs for PE100 material that reduce the energy consumption and the loss in pipe and fitting molding process are increasing.

To reduce the energy consumption, or to improve the energy efficiency of the molding, improvement of the flowability of the material is necessary. Easier flow material, which means the low viscosity at the molding shear rate, can reduce the motor load, material temperature and material pressure. Low motor load directly leads to the reduction of the energy consumption. Low material temperature reduces the cooling energy and time, so it has the possibility to increase the production speed. And low material temperature also can contribute to decrease the risk of processing defects such as burn particles and die drool. Low material pressure can lead to the extended life time of machine and mold. All these improvements mentioned above also lead to production cost reduction.

Regarding the injection molded fittings, the poor processability of conventional PE100 material has been a big issue. Low flowability of the material makes the surface finish of the fittings very bad and often causes warpage problems, reducing the design freedom of the fittings. So, PE100 material with high flowability is now strongly required also from the view point of product quality of the fittings.

Although we stated the needs to improve the flowability of PE100 material, PE100 material of course must have durability and strength that are required by the standards (ISO 4437 for gas, ISO 4427 for water).

To keep or further increase reliability for PE100 material, new high flow PE100 material should have far higher values than those required in the standards, not just meeting the requirements. In Table 1, we summarize recent needs for PE100.

Table 1 Recent market needs and requirements for PE100 material

Market Needs	Material Property (Required)	Expected effects
Reliability	Sufficient SCG /RCP	● Increase of product reliability ● Meeting new installation methods (No-sand, No-dig etc.)
Production efficiency	Good processability	● Energy saving during molding ● Loss reduction ● Flexibility increase of the fitting design ● Life time extension of molding machine and mold

NEW MATERIAL DEVELOPMENT

To meet recent needs for PE100 material, we started the development of new PE100 grade which has an excellent balance between durability and processability.

Generally, PE100 material for pressure pipe application is bimodal product which consists of 2 components, low density high molecular weight component (HMWC) and high density low molecular weight component (LMWC). The higher the ratio of HMWC is to improve strength and durability of the material, the poorer the material flowability becomes. Oppositely, the higher the ratio of LMWC is, the lower the product durability becomes. For these reasons, it is not easy to increase flowability of PE100 material keeping its excellent strength and durability.

In our previous study which we reported in PPXⅢ, we mentioned that concentrating co-monomer in HMWC and distributing co-monomer evenly within the molecule are two important factors in order to develop excellent durability material[2]. To realize such molecular architecture, we also mentioned our Advanced Multi-modal Slurry Loop Process (AMSLP) and our high performance catalyst. AMSLP is our original process with 3 cascade reactors and is capable of precise control of each molecular weight component. And our high performance catalyst has a feature of high co-polymerization ability and even co-monomer distribution in PE molecule. In order to achieve an excellent balance, we studied more precisely the relationship between molecular architecture and polymer properties, using AMSLP and our high performance catalyst.

In this study, we used C_L/C_H and Tβδ/Tδδ/C as indicators to show the state of co-monomer incorporation which affect the durability of the material. C_L/C_H indicates the co-monomer concentration ratio of LMWC to HMWC. We measured the C_H directly by using C-13 NMR[3]. Regarding C_L, we calculated the value using C_H and co-monomer concentration of the whole polymer. The lower C_L/C_H value is, the more the co-monomer is concentrated in the HMWC. Tβδ/Tδδ/C is also calculated from the C-13 NMR spectrum[4,5]. As shown in Fig. 1, Tβδ means the number of the successive incorporation of two co-monomers, calculated from the height of 36.0 ppm peak. Tδδ means the number of the isolated co-monomer incorporation, calculated from the height of 38.1 ppm peak. C means the co-monomer content of the whole polymer. The lower Tβδ/Tδδ/C value is, the more evenly the co-monomer is incorporated in PE molecular chain.

As a result of further study and refining of the AMSLP technology, we developed a new PE100 grade (NOVATEC™ HD HE222W) which has an excellent balance between durability and processability. Table 2 shows the summery of our study on the molecular architecture. The SCG resistance was estimated with our evaluation method, Accelerated Full Notch Creep Test (FNCT). The details of this test method are shown in Fig. 2. This test result has a good correlation with notch pipe test (NPT)[6] result measured according to ISO 13479. Fig. 3 shows the correlation between Accelerated FNCT and NPT.

In Table 2, PE-1 is a bi-modal material produced using conventional 2 staged cascade reactor, whose HLMFR is 9g/10min. NOVATEC™ HD HE212W is a PE100 material produced using AMSLP with excellent SCG resistance we previously reported in PPXⅢ, whose HLMFR is the same as that of PE-1. As shown in Table 2, both C_L/C_H and Tβδ/Tδδ/C of NOVATEC™ HD HE212W are lower than those of PE-1 , this means that co-monomer of NOVATEC™ HD HE212W is more concentrated in HMWC and more evenly incorporated in PE molecular chain than those of PE-1. We think that this difference is the reason why Accelerated FNCT value of NOVATEC™ HD HE212W (550h) is nearly 8 times higher than that of PE-1 (70h).

In the development of NOVATEC™ HD HE222W, we tried to enhance the concentration of co-monomer in HMWC, or tried to reduce the C_L/C_H value, by optimally adjusting the polymer content, molecular weight and co-monomer content of each of the 3 stages. As shown in Table 2, C_L/C_H value of NOVATEC™ HD HE222W (0.08) is the lowest in these three materials. We think that this low C_L/C_H makes it possible for NOVATEC™ HD HE222W to have high Accelerated FNCT value of 350h which is 5 times higher than that of PE-1, in spite of high HLMFR (18g/10min) of NOVATEC™ HD HE222W which is twice of that of conventional bi-modal PE (PE-1).

Table 2 Summary of our molecular architecture study

		PE-1	NOVATEC™ HD HE212W	NOVATEC™ HD HE222W
Process	—	2-stage polymerization	AMSLP	AMSLP
Catalyst	—	High performance catalyst	High performance catalyst	High performance catalyst
HLMFR	g/10min	9	9	18
Density	kg/m^3	950	948	950
Co-monomer	-	Hexene-1	Hexene-1	Hexene-1
C (co-monomer concentration)	mol%	0.42	0.55	0.42
C_L/C_H	-	0.40	0.16	0.07
Tβδ/Tδδ/C	-	0.14	0.09	0.08
Accelerated FNCT	h	70	550	350

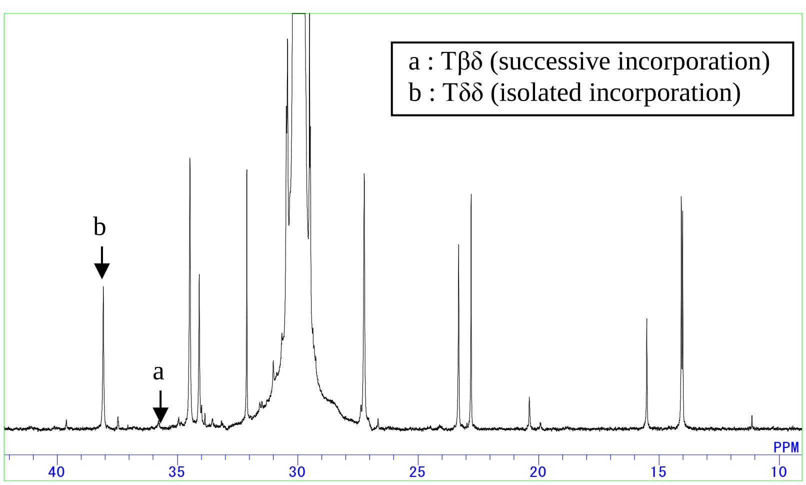

Fig. 1 C-13 NMR spectrum

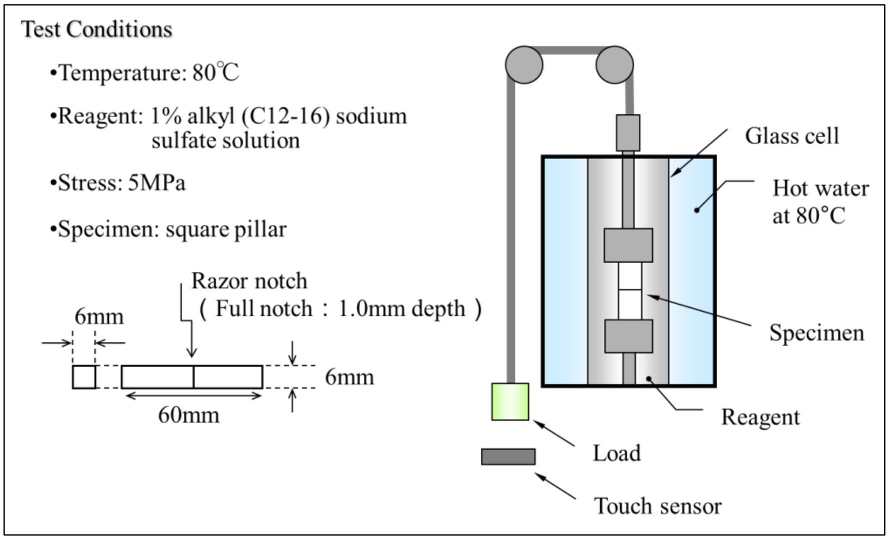

Fig. 2 Accelerated FNCT

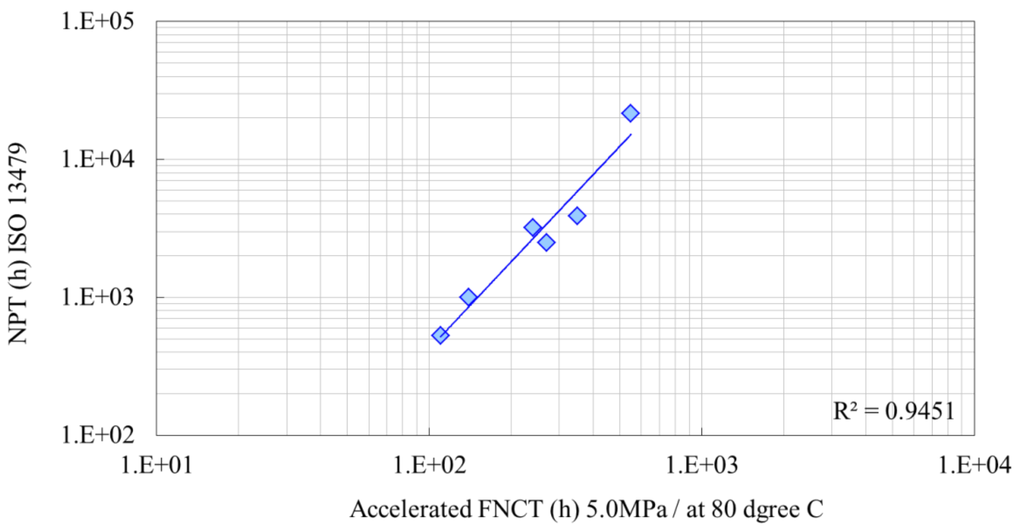

Fig. 3 Relationship between Accelerated FNCT and NPT

EVALUATION RESULTS OF NEW HIGH FLOW PE100 (NOVATEC^{TM} HD HE222W)

We evaluated practical properties required for PE100 material and processability for pipe extrusion and injection molding of NOVATEC^{TM} HD HE222W.

In Table 3, we summarize the evaluation results of this New PE100 grade (NOVATEC^{TM} HD HE222W) together with those of our other commercial PE100 grades. NOVATEC^{TM} HD HE212W is also PE100 material produced using AMSLP, whose HLMFR is 9 g/10min and its SCG resistance is the most excellent. PE-A and PE-B are our previous PE100 grades produced using conventional 2 staged cascade reactor. HLMFR of PE-A is 17g/10min, nearly the same level of NOVATEC^{TM} HD HE222W. HLMFR of PE-B is 9 g/10min, the same as that of NOVATEC^{TM} HD HE212W.

Fig. 4 shows the shear rate dependences of viscosity. These data were measured using capillary rheometer (test temperature : 190 degree C, capillary diameter (D) : 1.53mm ϕ , length (L) : 25.43mm). The melt viscosity of NOVATEC^{TM} HD HE222W in high shear region is the lowest among them. These results show that NOVATEC^{TM} HD HE222W is an appropriate material for especially injection molding.

Accelerated FNCT (specimens were made by press molding) and NPT were performed for estimation of the SCG resistance. It turned out that NOVATEC^{TM} HD HE222W excels the other PE100 materials produced by conventional technology in the SCG resistance in spite of its highest HLMFR of 18g/10min.

Table 3 Typical properties of NOVATEC^{TM} HD HE222W compared with commercial PE100 materials

Property	Unit	Method	NOVATEC^{TM} HD HE222W	NOVATEC^{TM} HD HE212W	Commercial PE-A	Commercial PE-B
HLMFR	g/10min	ISO 1133	18	9	17	9
FRR(21.6/2.16)	-	ISO 1133	150	180	140	180
Density	kg/m^3	ISO 1183	950	948	949	950
Class	—	—	PE100	PE100	PE100	PE100
Process	—	—	AMSLP	AMSLP	2-stage polymerization	2-stage polymerization
Notch pipe test	h	ISO 13479	3,900*	21,700*	2,500 **	—
Accelerated FNCT	h	-	350	550	270	130
Charpy impact strength at 23 degree C	kJ/m^2	ISO 179	22	34	20	20
Charpy impact strength at -20 degree C	kJ/m^2	ISO 179	9	19	9	10
RCP-S4	bar	ISO 13477	—	> 25 *	> 16 **	—
Co-monomer	-	-	Hexene-1	Hexene-1	Hexene-1	Butene-1

* determined at EXOVA ** determined at Kiwa Gastec Certification

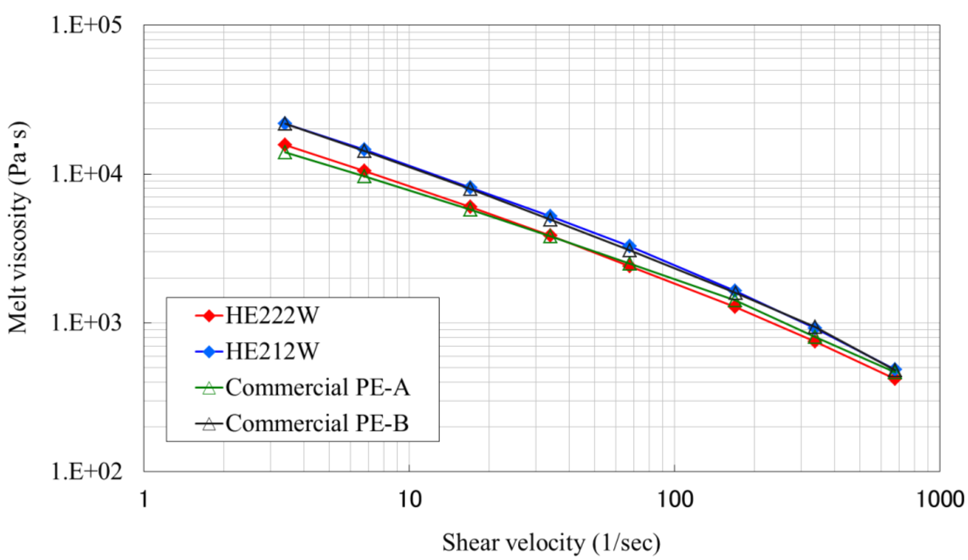

Fig. 4 Shear rate dependence of viscosity at 190 degree C

Although HLMFR of NOVATEC™ HD HE222W is very high as PE100 material, the value of the NPT is 7 times higher than the required value (500h) in water and gas pipe application (ISO 4427[7]/4437[8]). This result indicates the balance between the durability and the flowability of NOVATEC™ HD HE222W is excellent. Fig. 5 shows the result of hydrostatic strength measured according to ISO 9080[9]. There was no brittle failure at all temperatures until 10,000h. And break time of NOVATEC™ HD HE222W at 20 degree C under 12.4 MPa hoop stress was over 500h. This result shows that NOVATEC™ HD HE222W has enough durability as well.

Regarding rapid crack propagation (RCP) properties of NOVATEC™ HD HE222W, although we have not yet carried out the test, comparing the Charpy impact strength of NOVATEC™ HD HE222W with that of PE-A, we consider that S4 (small-scale steady-state) RCP[10] performance of NOVATEC™ HD HE222W will be the same level (>16 bar, at 0 degree C) as that of PE-A[11].

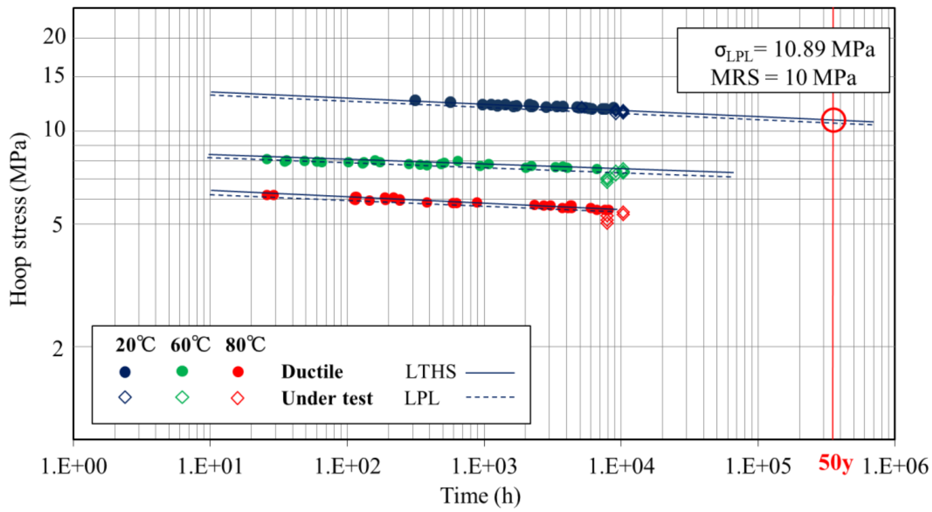

Fig. 5 Hydrostatic strength data of NOVATEC™ HD HE222W : determined at EXOVA

We evaluated the extrusion properties using the pipe extrusion machine. The test was carried out with 45mm screw diameter, 33 L/D Krauss-Maffei pipe molding machine at 200 degree C. Fig. 6 shows the relationship between output and motor current. The motor current value of NOVATEC™ HD HE222W is lower than those of conventional PE100 materials. Fig. 7 shows the relationship between output and molding pressure. The molding pressure value of NOVATEC™ HD HE222W at the same output is extremely small compared with those of conventional PE100 materials. From these results, we think that NOVATEC™ HD HE222W could be extruded at lower temperature compared with other conventional PE100 materials due to its superior high flowability. As the merits of molding at low temperature, reduction of extrusion defects such as burn particles and die drool, and increase of production rate by shortening cooling period could be expected.

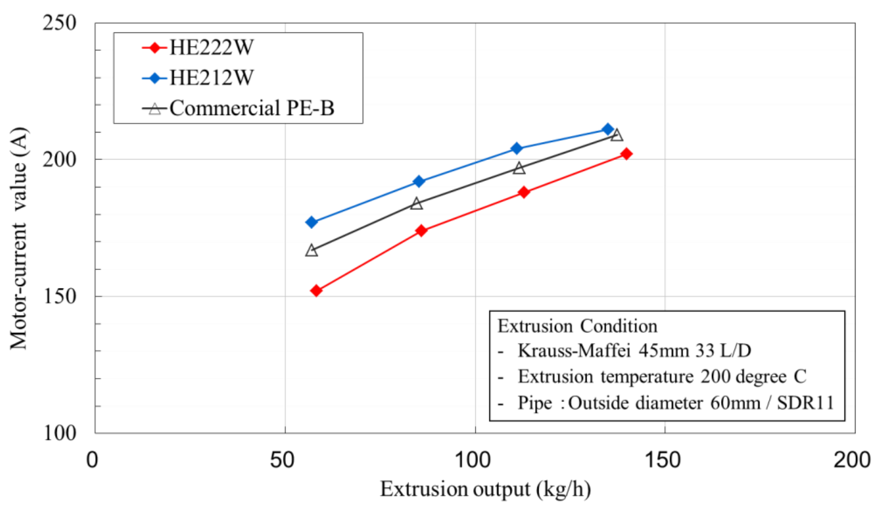

Fig. 6 Processability data-1: relationship between output and motor-current

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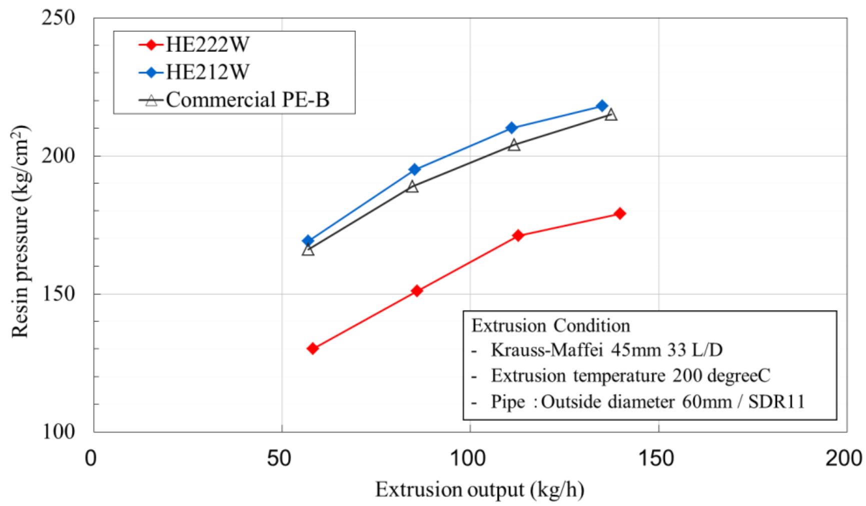


Fig. 7 Processability data-2: relationship between output and material pressure

We evaluated the processability for injection molding by the spiral flow test. The data of this test are shown as the flow length at respective injection temperature. We used FANUC injection molding machine and the Archimedean spiral mold (10mm width, 2mm thickness, 2,000mm maximum length, mold temperature at 40 degree C). Fig. 8 shows the spiral flow test specimen. The results are shown in Fig. 9. The spiral flow length of NOVATEC™ HD HE222W at 230 degree C is 30% longer than that of the NOVATEC™ HD HE212W whose HLMFR is 9g/10min, and 10% longer than that of PE-A whose HLMFR is 17g/10min. Furthermore, the length of NOVATEC™ HD HE222W at 210 degree C is the same as or longer than that of the commercial PE-A at 230 degree C. From these results, we think that NOVATEC™ HD HE222W could reduce cycle time and defects rate through lower processing temperature.
Furthermore it is expected that complicated shape fittings which was not able to be designed by the conventional PE100 materials could be realized by NOVATEC™ HD HE222W.

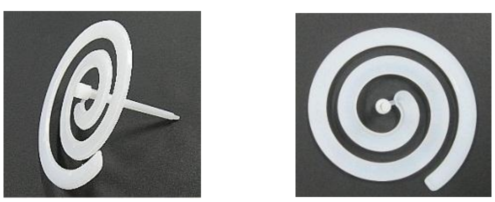


Fig. 8 Spiral flow specimen

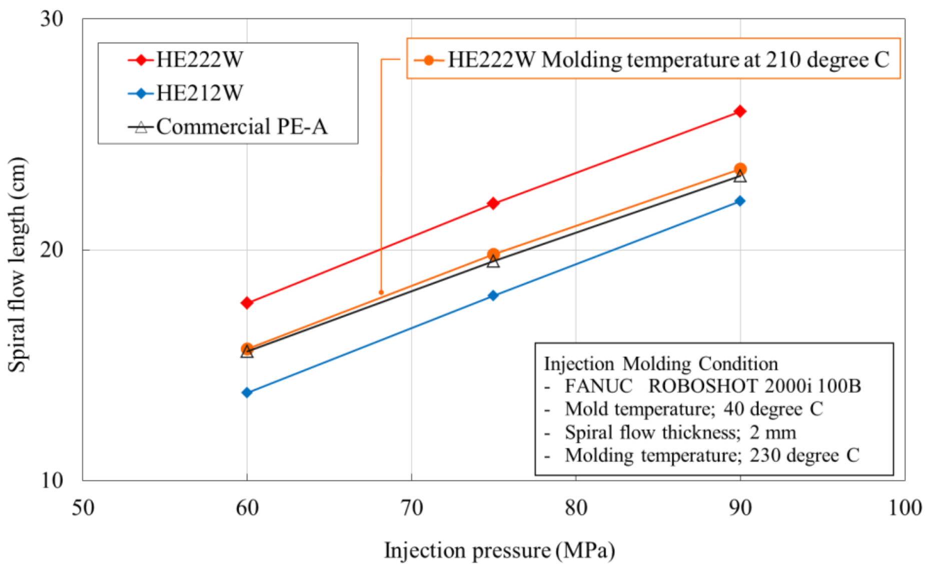
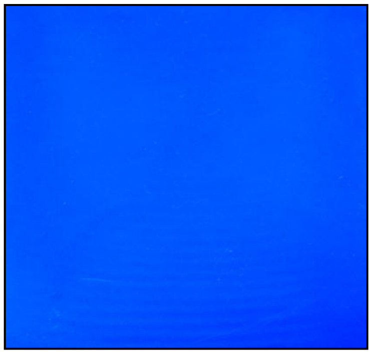


Fig. 9 Processability data-3: relationship between injection pressure and spiral flow length

Fig.10 shows the surface of the injection molded flat plate (2mm thickness) made from NOVATEC™ HD HE222W and PE-B (HLMFR 9g/10min). In case of NOVATEC™ HD HE222W, flow mark does not appear on the surface. This result suggests that NOVATEC™ HD HE222W could give better surface finish of fittings than conventional PE100 material.

NOVATEC™ HD HE222W



Commercial PE-B

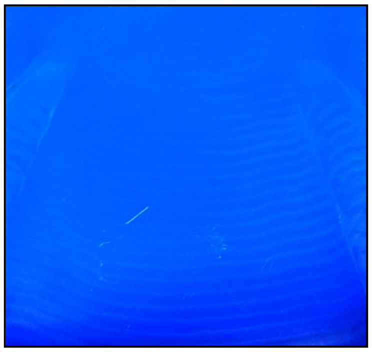


Fig. 10 Comparison of injection molded plate surface

CONCLUSION

By precise control of molecular architecture using AMSLP, we succeeded to develop new high flow PE100 material (NOVATEC™ HD HE222W) with excellent balance between durability and processability. In spite of its high HLMFR of 18g/10min, it has the durability far exceeding the requirements of ISO 4427/4437, and also can exceed the property requirements defined by PE100+ association.

In Table 4, we summarize the effects and merits gained from using NOVATEC™ HE222W.

We hope that NOVATEC™ HD HE222W will play a part to improve the production efficiency of PE pipe industry and contribute to the establishment of sustainable society.

Table 4 Expected effects and merits by NOVATEC™ HD HE222W

Extrusion molding	Injection molding
Improved effects ○ Reduction of material temperature ○ Reduction of motor load ○ Reduction of material pressure ○ Increase of through-put	Improved effects ○ Reduction of material temperature ○ Reduction of injection pressure ○ Increase in the flow length ○ Improvement of surface finish
Merits ○ Energy saving ○ Defects reduction by low-temperature molding ○ Increase in production rate ○ Production cost reduction	Merits ○ Energy saving ○ Defects reduction by low-temperature molding ○ Increase in production rate ○ Increase of design freedom of fittings ○ Extended life of machine and mold ○ Production cost reduction

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ANNEX A

PE 100+ Association required quality of materials

Property	Test Method	PE 100+ Association requirements
Creep Rupture Strength	Pressure test at20°C and 12.4 MPa	≧200（h）
Stress Crack Resistance	Pipe notch test at 80°C and 9.2 bar	≧500（h）
Resistance to Rapid Crack Propagation	S4 Test at 0°C	Pc≧10 bar