

High performance PE100 Resin with extraordinary resistance to Slow Crack Growth

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Abstract

Polyethylene, especially PE100 Resin has been steadily increasing its use in pressure pipes for water and gas based on its superior property balance. Of all the properties required for PE100, when we consider the defects on the pipe surface and the stress concentrations on the fitting of complicated shape, the most important for the lifetime of pipe should be the resistance to Slow Crack Growth (SCG). Recent requirements for cost reduction by no-dig or no-sand installation have been enhancing the need for the improvement of SCG resistance. Requirements to Rapid Crack Propagation (RCP) for higher operating pressure and no sag for large diameter - thick wall pipe are also increasing. To meet these requirements, we investigated the relationship between molecular architecture and resin properties in detail, and we optimized the molecular weight, molecular weight distribution, co-monomer, co-monomer distribution using our advanced multi-modal polymerization process and high activity catalyst. Our new PE100 resin has the Notch Pipe Test result of more than 17,000 h. This value is far above the typical values of PE100 resins so far on the market and more than 3 times greater than the requirement for PEX pipe. It has the RCP-S4 value of more than 25 bar, and its designed high shear sensitivity also gives a good no sag property without sacrificing extrusion/injection processing properties.

We believe that continuous improvements of resin performance will help PE pipe to continue to expand, meeting more demanding new installation methods and contributing to enhance the safety margin of the PE pipe system.

Introduction

Polyethylene(PE) has already established its position as a major material for many pipe applications, such as gas and water distributions (pressure pipes), sewerage, drainage and conduit, based on its excellent characteristics such as light weight/ flexibility for easy handling and chemical stability for corrosion resistance. The strength of PE pipe line system to the earthquake according to its ability to follow the ground movement and excellent fusion-welding strength is now well acknowledged. In Japan, there have been several strong earthquakes with the magnitude of more than 6 such as the

Great Hanshin-Awaji earthquake (Magnitude 7.3, 1995) and the Niigata-ken Chuetsu earthquake (Magnitude of 6.8, 2004). Although there were a lot of damages observed to iron, steel and PVC pipes in those earthquakes, there was no report of the damage to the PE gas and water pipe line system. Therefore, the usage of PE pipes to the lifelines like water and gas is increasing year after year also in Japan.

PE for pipes, especially PE100 resin, has been steadily increasing its use all over the world and is expected to grow further. Together with the spreading of PE100 resin, the requirements for cost competitive installation methods like no-dig or no-sand methods are also increasing. In these installation methods, however, we can not avoid the surface defect by scratching and the concentrated local stress by stone or something like that in the backfill material. These defect and stress concentration can give the pipe more stress than anticipated and may cause the failure of the pipe, if the material's resistance to stress crack or slow crack growth (SCG) is not strong enough. Electro-fusion (EF) fitting is widespread for pressure pipe systems, because the operation is easy and the reliability on the fusion-welding strength is high. However, the complicated shape of the fitting itself and the possible notch shape at the welded part may cause stress concentrations and lead to the failure, if the design of the fitting is not appropriate and the resistance of the material to SCG is not sufficient. When we consider these influences that deteriorate the system, the resistance to SCG is extremely important for the life time of the actual pipe line system.

The SCG resistance of the material can be evaluated by several other methods like PENT¹ and FNCT², however, Notch Pipe Test (NPT) according to ISO13479³ is used for gas and water applications (ISO 4437⁴ for gas, ISO 4427⁵ for water) as the most reliable evaluation method considering the actual usage of the pipe. The value now required for gas and water is more than 165 h. There are a lot of PE100 resins that meet the criteria of ISO 9080⁶, however, the SCG value of each PE100 resin varies. Many works have been carried out by many resin manufacturers so far to improve the SCG properties. And now, some of the PE100 resins have the SCG values far beyond 165 h.

Beside the SCG, the requirements to Rapid Crack Propagation (RCP) for higher operating pressure and no sag property for large diameter - thick wall pipe are also increasing. To meet these requirements, we investigated the relationship between molecular architecture like molecular weight (MW), molecular weight distribution (MWD), co-monomer, co-monomer distribution and resin properties in detail, and tried to find the best balance between mechanical properties and processability. To achieve the desired molecular architecture, we tried to optimize the polymerization conditions using our advanced multi-modal polymerization process and high activity catalyst.

Relationship between Molecular Architecture and Polymer Properties

The crack propagation of SCG is considered to happen between crystalline lamellas and the rate of SCG is considered to relate with the rate of disentanglement of tie-molecules between crystalline lamellas. So, increasing the number of tie-molecules to delay the disentanglement is considered to be the key point to improve the SCG. It is generally understood that increasing the co-monomer content improves the SCG, or, increases the number of tie-molecules. But, it also reduces the stiffness of the material. PE100 requires both high stiffness and high durability. The molecular architecture that realizes the good property balance is required. Y. L. Huang et al.⁷ calculated the number of tie-molecules based on the assumption that molecules with larger end to end distance than the critical distance ($2L_c + L_a$), where L_c means the thickness of the crystal and L_a means the thickness of the amorphous layer between the crystals, will form a Tie-molecule. Using this theory, we can get the guideline for desired molecular architecture that provides more tie-molecules at the same co-monomer content. To concentrate the co-monomer in the higher molecular portion and to distribute the co-monomer evenly within the molecule are two important factors.⁸

Table 1 shows the summary of the relationship between bi-modal molecular architecture and properties that are required for PE pipe material. Within these relationships, to find the best balance and to realize the desired molecular architecture by adjusting the polymerization conditions are our purpose. Today, bi-modal or multi-modal process that produces high molecular weight co-polymer and low molecular weight homo-polymer in a series of reactors is usually used. Fig.1 shows the scheme of molecular distribution of a bi-modal PE and the basic design concepts.

Property	Component ratio		Molecular weight distribution (MWD)	
	High molecular weight component (HMWC)	Low molecular weight component (LMWC)	Narrow	Broad
Higher creep performance	+	-	-	+
Higher resistance of ESC or SCG	+	-	-	+
Higher tensile strength	+	-		
Higher impact strength	+	-	+	-
Higher stiffness		+		
Better processability	-	+	-	+
Better external appearance	-		+	-
Lower shrinkage	-			-

Note: +: positive effect -: negative effect

Table 1 Relationship between basic bi-modal molecular architecture and polymer properties.

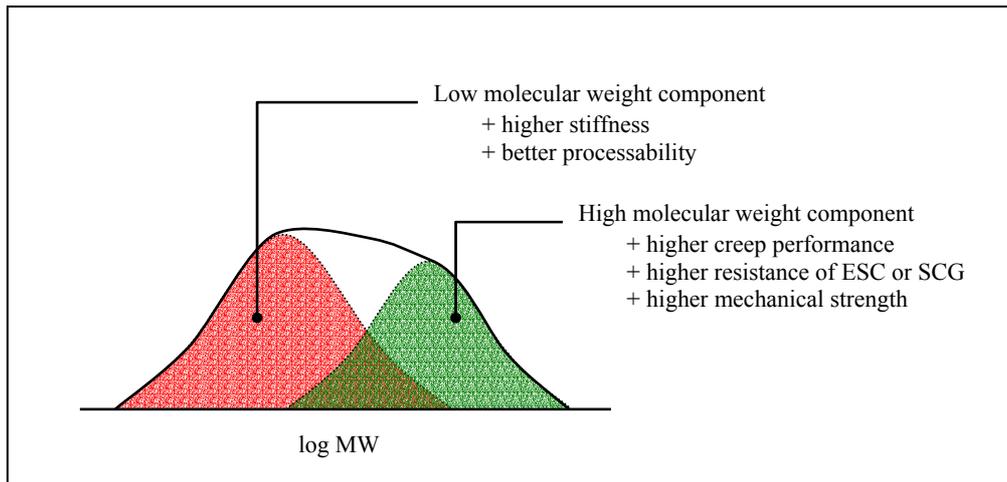


Fig. 1 Scheme of molecular weight distribution of a bimodal PE

Polymerization: Advanced Multi-modal Slurry Loop Process

Molecular Weight (MW) and Co-monomer Content, which are main factors to affect polymer properties, are controlled by the polymerization conditions like polymerization temperature, polymerization pressure, residence time, hydrogen partial pressure, co-monomer concentration and so on. In multi-modal process, each condition is controlled independently in each reactor. Precise control of those factors in each reactor is the key point to obtain the polymer of desired molecular architecture. We carried out the development of PE100 material with excellent SCG resistance using our Advanced Multi-modal Slurry Loop Process (AMSLP) and our high performance Ziegler-Natta Catalyst.

In multi-modal or cascade reactor process, High Molecular Weight Component (HMWC) and Low Molecular Weight Component (LMWC) are polymerized in a series, however, the order of the polymerization is different by manufactures or polymerization processes. In case of the polymerization that produce the LMWC first, the possibility of poor dispersion of HMWC, Gel or Fish Eye, is higher than that of the opposite polymerization order, when we try to increase the MW difference between the two components to get a good processability and a good stiffness and SCG balance. So, we used the polymerization order that produce the HMWC first. Not only the MW difference between the two components but also the ratio of HMWC and LMWC affects the dispersion of HMWC. Fig. 2 shows the bad example of HMWC dispersion. Optimization of MW and ratio of each component is very important.



Fig. 2 The inner wall of the pipe made from the material which has a poor dispersion of HMWC

As we mentioned above, concentrating the co-monomer in the higher molecular portion and distributing the co-monomer evenly within the molecule are two important factors in order to get excellent SCG resistant PE100 material. In other words, catalyst and polymerization conditions that increase the capability of co-polymerization in the HMWC production, that increase the density of LMWC as high as possible and that increase the evenness of co-monomer incorporation are essential. We investigated catalyst, process and polymerization conditions to realize these criteria. Table 2 shows the summary of our investigation. In the table 2, C_L/C_H means the ratio of co-monomer content of LMWC to HMWC. In this experiment, we used hexene as co-monomer. We measured the C_H directly using C-13 NMR spectrum^{9, 10} of HMWC. Regarding C_L , we calculated the value using C_H and that value of whole polymer. The lower the value is, the more the co-monomer is concentrated in the HMWC.

We calculated $T\beta\delta/T\delta\delta/C$ as the figure that indicates the evenness of the co-monomer incorporation. As shown in Fig. 3, $T\beta\delta$ calculated from the height of 36.0 ppm peak means the number of successive incorporation of two co-monomers and $T\delta\delta$ calculated from the height of 38.1 ppm peak means the number of the isolated incorporation of co-monomer.¹¹ And C means the co-monomer content of the polymer. The lower the value is, the more evenly the co-monomer is incorporated. PE-2 shows the result of polymerization condition optimization to increase the capability of co-polymerization in the HMWC production and increase the evenness of co-monomer incorporation. Although the whole polymer's HLMFR (MW) and density of PE-1 and PE-2 are nearly the same, the values of C_L/C_H and $T\beta\delta/T\delta\delta/C$ of the two polymers are different. The lower C_L/C_H and $T\beta\delta/T\delta\delta/C$ values of PE-2 means that PE-2 has more co-monomer in HMWC and has more evenly incorporated co-monomer than PE-1. As the result of the difference of molecular architectures of the two polymers, PE-2 has nearly 4 times higher value of Notched Lander ESCR, which we use as a screening test method for SCG at our laboratory. The details of the test method are shown in Fig. 4.

PE-3 is produced using the three cascade slurry loop reactor process, "Advanced Multi-modal Slurry Loop Process (AMSLP)", producing the same specification HMWC in the first and second reactors, and then LMWC in the third reactor. We produced PE-3 with the same ratio of HMWC to LMWC as that of PE-1 and PE-2, and adjusted the polymerization condition to get the same HLMFR and

density as a whole polymer after pelletizing. PE-3 has even lower values of C_L/C_H and $T\beta\delta/T\delta\delta/C$ than those of PE-2, and as a result it has even higher value of Notched Lander ESCR compared to PE-2. As these results show, we could confirm that fine control of the molecular architecture by precise and sophisticated polymerization can further improve SCG resistance.

		PE-1	PE-2	PE-3
After 1st reactor				
HLMFR	g/10min	0.16	0.19	0.16
Density	kg/m ³	929	927	923
Comonomer	-	Hexene	Hexene	Hexene
Polymerization Percentage at 1st reactor	%	45	45	23
After 2nd reactor				
HLMFR	g/10min	12	13	0.14
Density	kg/m ³	949	949	923
Comonomer	-			Hexene
Polymerization Percentage at 2nd reactor	%	55	55	23
After 3rd reactor				
HLMFR	g/10min			15
Density	kg/m ³			948
Polymerization Percentage at 3rd reactor	%			54
After palletizing				
HLMFR	g/10min	9.0	9.9	9.4
Density	kg/m ³	949	949	948
C_L/C_H	-	0.40	0.18	0.16
$T\beta\delta/T\delta\delta/C$	-	0.14	0.11	0.09
Notched Lander ESCR	h	70	300	533

Table 2 Typical properties of the investigated materials

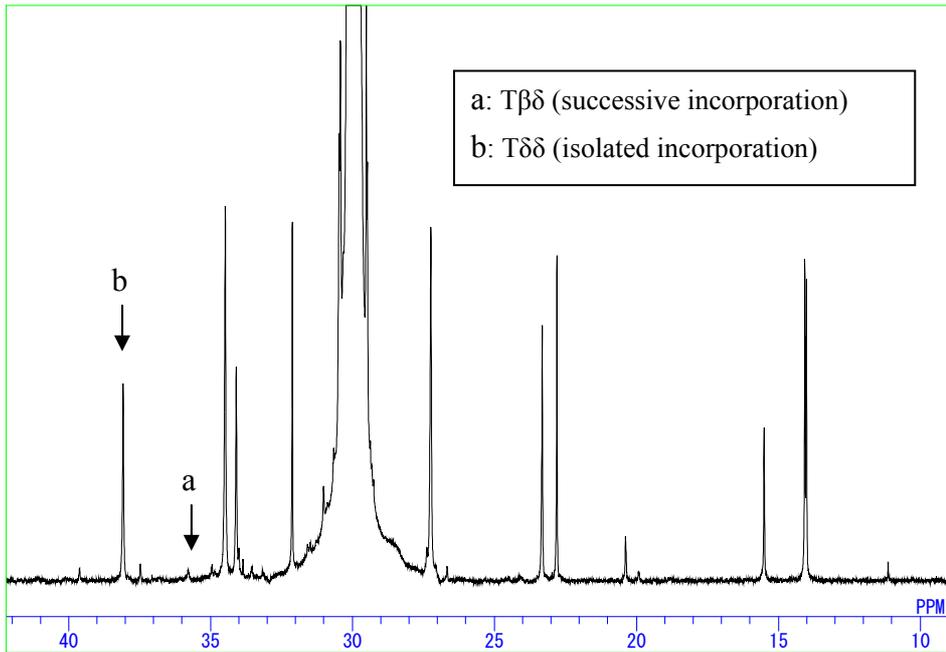


Fig. 3 ^{13}C -NMR spectrum

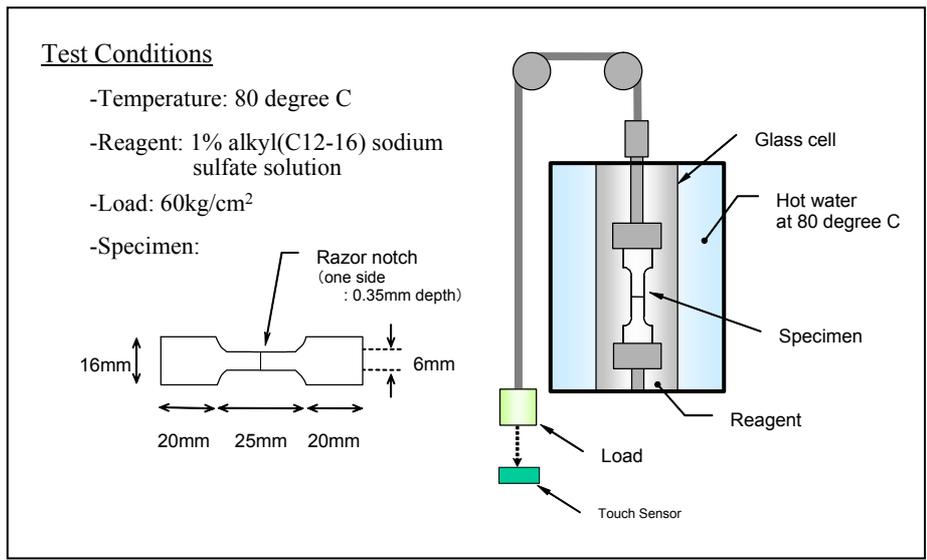


Fig. 4 Notched Lander ESCR test

Evaluation result of new PE100 material

Based on the results we mentioned in the earlier chapter, we developed new PE100 grade (New-PE100) using our Advanced Multi-modal Slurry Loop Process (AMSLP). In Table 3, we summarize the evaluation results of this New-PE100 together with those of our previous PE100

grades (PE100-A, PE100-B). In these results, the particularly notable feature is the SCG resistance of New PE100. We evaluated the SCG resistance by Notched Pipe Test (NPT) according to ISO 13479 using 110mm outside diameter and 10mm thickness pipe, at the test temperature of 80 degree C and inside pressure of 9.2 bar. NPT is now regarded as the most realistic method to evaluate the failure of surface scratched pipe.¹¹ This test was performed on 110mm SDR11 pipe using pressure of 9.2 bar at 80 degree C. New-PE100 designed to improve SCG performance did not rupture until 17,200h, though the performance of our previous PE100 grade (PE100-A) was less than 3,000h. The actual failure times of the 5 tested specimens were from 17,236 h to 24,186 h. This value is far beyond the now required value of 165h in gas pipe application (ISO 4437) and more than 3 times higher than the minimum required value for the PEX pipe (ISO 14531-1)¹³ that is often used with the no-dig installation methods because of it's superior SCG properties. Fig. 5 shows the stress dependence of NPT failure time. Compared with PE100-B, New-PE100 has higher hoop stress value at the same failure time level.

Fig. 6 shows the result of the hydrostatic strength test of New-PE100 according to ISO 9080.

There was no brittle failure at all temperatures during the test period. Fig. 7 shows the S4 (small-scale steady-state) rapid crack propagation (RCP) performance of New-PE100 according to ISO 13477¹⁴ using 110mm diameter and SDR11 pipes. We measured the critical pressure ($P_{c, S4}$), at which there is an abrupt transition from arrest to propagation of the initial crack changing the inside pressure level, at 0 degree C. Although we increased the inside pressure until 25 bar, New-PE100 showed no crack propagation. It shows that New-PE100 has enough RCP strength for higher operating pressure and for larger diameter-thick wall pipes. This good RCP result is suggested by the excellent Charpy impact strength of New-PE100.

Property	Unit	Method	New-PE100	PE100-A	PE100-B
HLMFR	g/10min	ISO 1133	9	22	9
FRR(21.6/2.16)	-	ISO 1133	180	179	180
Density	kg/m ³	ISO 1183	948	949	950
Comonomer	-	-	Hexene	Hexene	Butene
Flexural modulus	MPa	ISO 178	1,100	1,100	1,200
Charpy impact strength at 23 degree C	kJ/m ²	ISO 179	37	22	25
Charpy impact strength at -20 degree C	kJ/m ²	ISO 179	19	8	10
σ_{LPL}	MPa	ISO 9080	10.22 * (PE100)	10.45 ** (PE100)	10.28 ** (PE100)
Notch pipe test	h	ISO 13479	> 17,200 *	2,500 **	-
RCP-S4	Bar	ISO 13477	> 25 *	> 16 **	-

* determined at Kiwa Gastec Certification

** determined at Bodycote Polymer

Table 3 Evaluation results of New-PE100

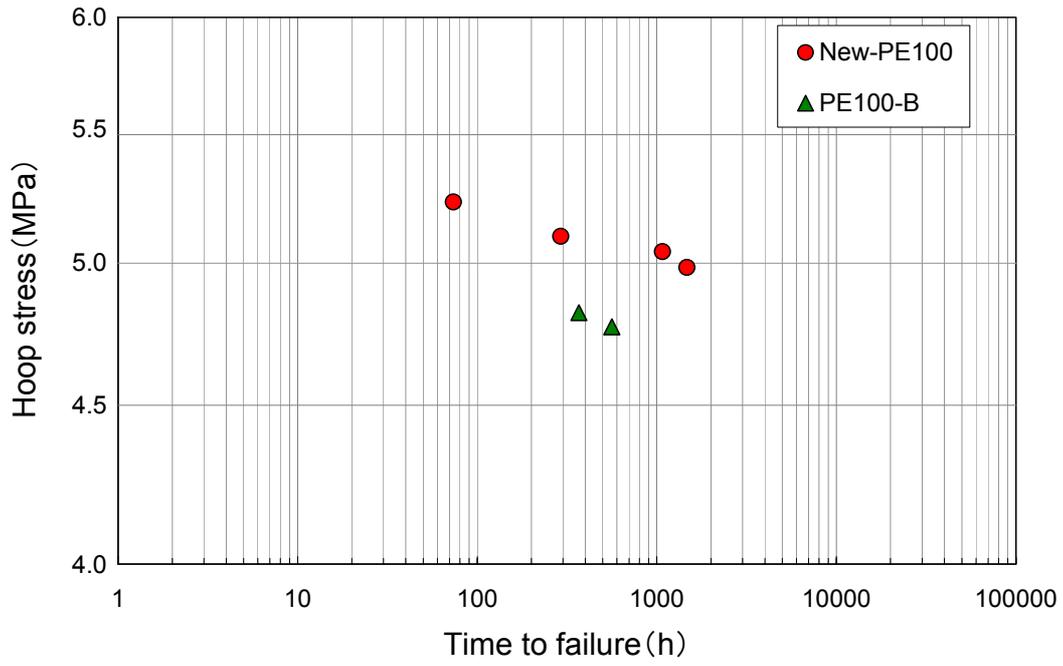
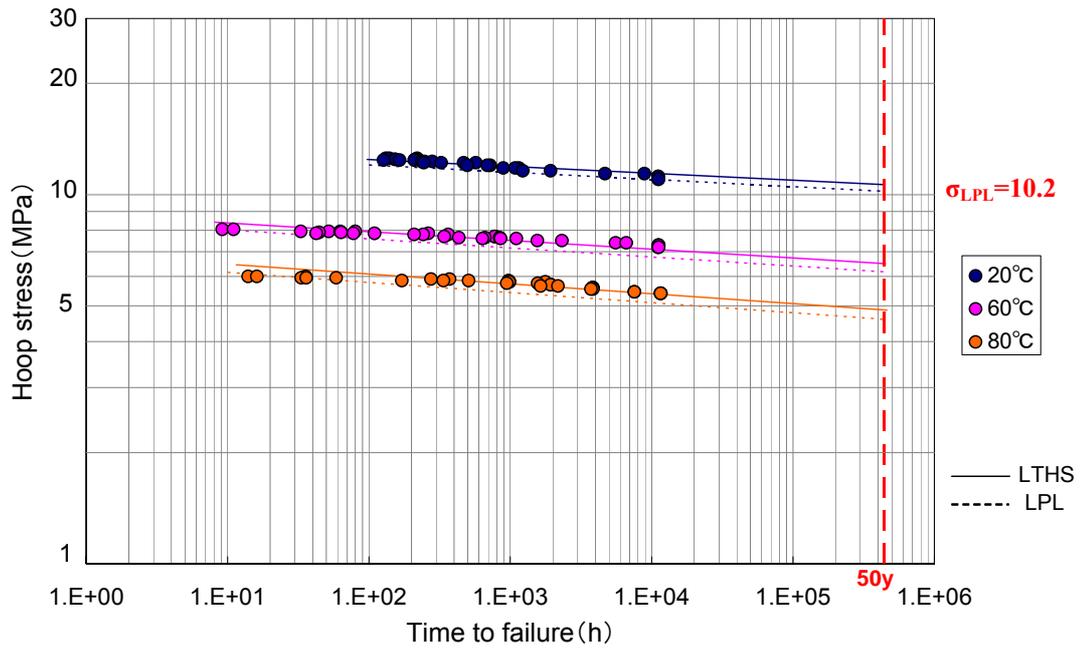


Fig. 5 Stress dependence of notched pipe test data



+ There has been no brittle failure during about 11,000h of testing at each temperature.

Fig. 6 Hydrostatic strength data: determined at Kiwa Gastec Certification

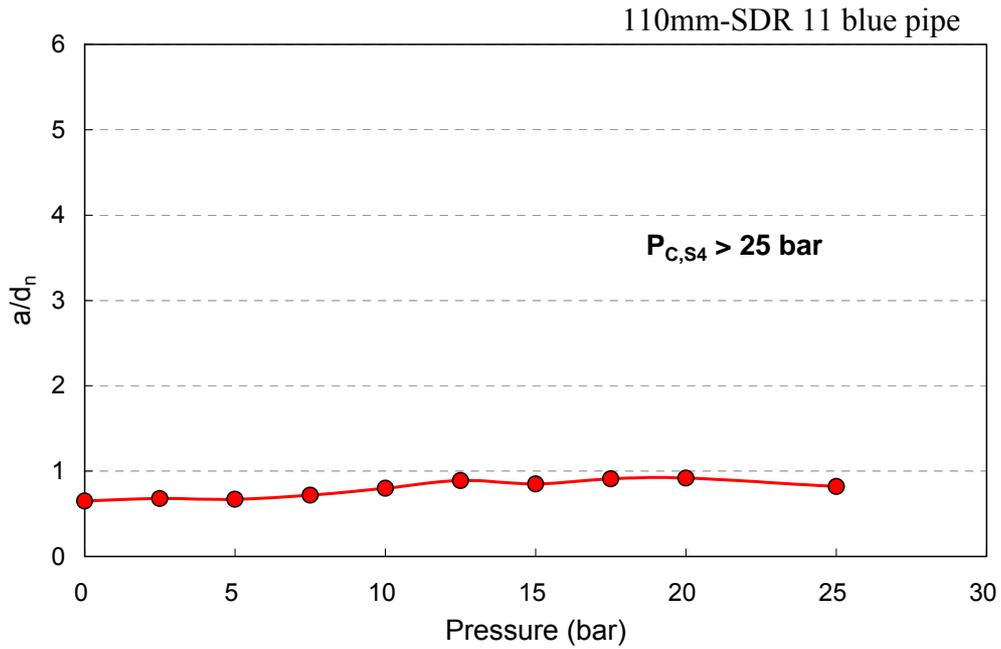


Fig. 7 Rapid Crack Propagation (S4 test) data: determined at Kiwa Gastec Certification

Regarding the processability, Fig. 8 shows the dynamic shear viscosity of New-PE100 at 190 degree C compared with PE100-B. We improved the no-sag and the extrusion properties of New-PE100 by giving it high shear sensitivity with very high viscosity at low frequency region.

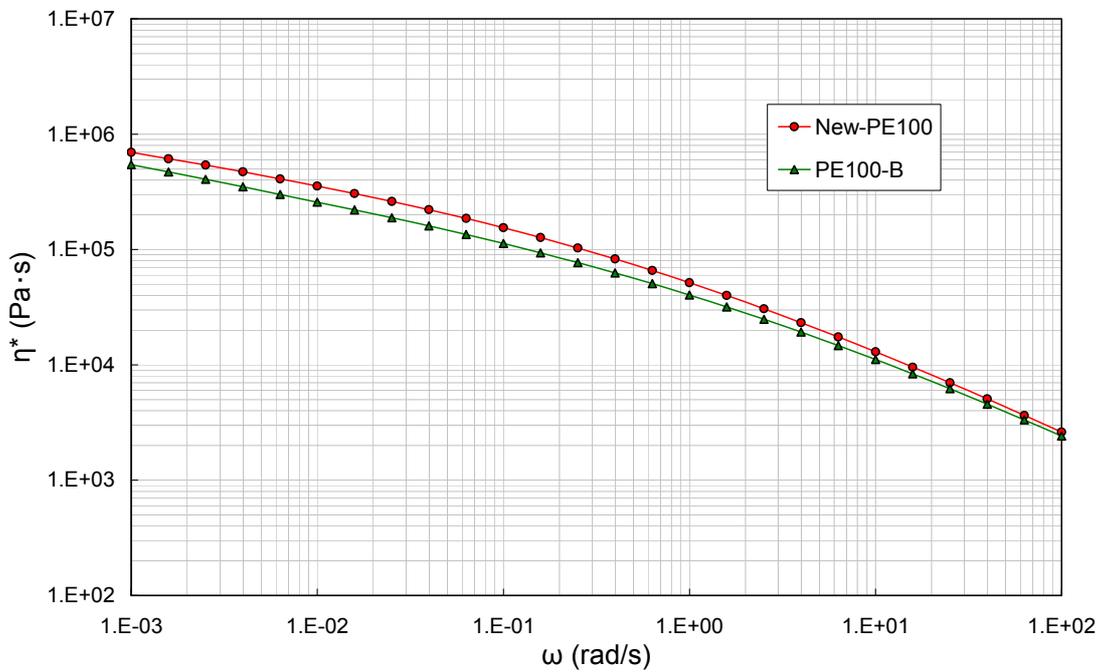


Fig. 8 Dynamic shear viscosity data at 190 degree C

We evaluated extrusion properties, producing 110mm diameter SDR11 pipes by the temperature pre-setting of 200 degree C. We used 45mm screw diameter, 33 L/D Krauss-Maffei pipe molding machine for the evaluation. Fig. 9 shows the relationship between screw speed and output. Fig. 10 shows the relationship between output and resin temperature. As shown in Fig. 9 and Fig. 10, New-PE100 has nearly the same extrusion properties as those of PE100-B.

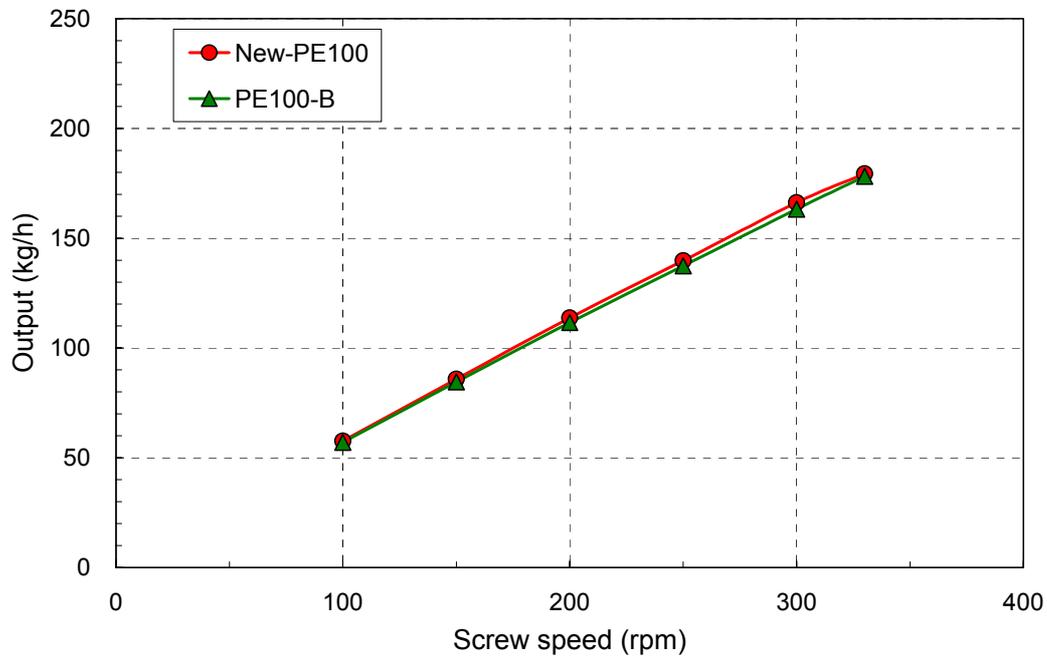


Fig. 9 Processability data-1: relationship between output and screw speed

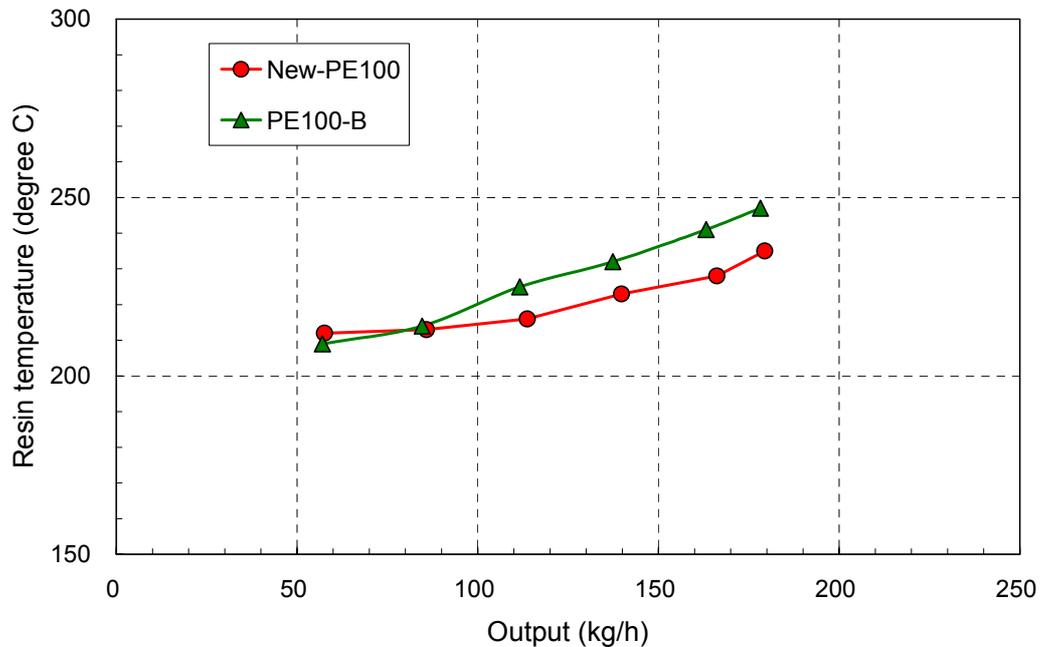


Fig. 10 Processability data-2: relationship between resin temperature and output

Conclusion

The efforts to improve PE100 or to develop higher rating material like PE125 are continuing in many PE manufactures to meet more demanding new installation methods and to contribute to enhancing the safety margin of the PE pipe-line system. As previous studies and this study clarify, what is important for excellent durability is to concentrate co-monomer in HMWC and distribute them as evenly as possible. We could achieve such molecular architecture by precise and sophisticated polymerization control and develop new PE100 with excellent SCG resistance using our 3 cascade-reactor process, AMSLP, and our high performance Ziegler-Natta catalyst. We believe that continuous efforts of PE manufactures will further improve PE properties and will expand the possibility of PE in the pipe industry.

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