The Rheological Behavior of EPDM Nordel IP and POE Engage Produced by CGC and INSITE^{TM} Technology

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ABSTRACT: The rheological behavior of EPDM Nordel and POE Engage produced by CGC and INSITE^{TM} technology are studied with double capillary rheometer of constant speed type. It is indicated that the melt viscosity of EPDM Nordel IP 3745P is higher and the nonlinear fluidity is stronger compared with Nordel IP 3722P, because the molecular weight of Nordel IP 3745P is higher and the MWD is narrow. We compare the melt viscosity of POE Engage GPE8003 with that of Engage GPE8150, and indicate that the influence of temperature on viscosity of Engage GPE8003 is obvious and the influence of shear rate on viscosity of Engage GPE8150 is stronger, which was related to the octene percent in material. The melt slide at wall and the extrusion pressure vibration occurred with EPDM Nordel IP 3745P. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2847–2853, 2006

Key words: EPDM; POE; rheological properties; double capillary rheometers

INTRODUCTION

The structure and properties characteristics of POE produced by CGC

CGC activator is a new kind of MAO metal activator developed by DuPont Dow chemical company, it is a kind of complex constructed by cyclopentadienyl and a transition metal of IV subunit with the coordination bond, the angle between cyclopentadienyl, transition metal, and mixed atom (for example N) being no larger than 115° (see Fig. 1). This special structure made the activator center opened only for one direction in the space, so that it controlled the insertion of long chain monomer of copolymer during the polymerization. It provided the facilities of designing and controlling the polymer molecule structure, molecule weight distribution, long chain branch, and monomer combining percent, to make polymer with the special structure, form, and properties.[1–3]

DuPont Dow chemical company developed the EPDM Nordel IP and POE Engage with CGC activator and INSITE^{TM} technology, which are two kinds of polyolefin elastomer with high pureness component, strict structure and properties control, and good product uniformity.

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EPDM Nordel IP has the molecular chain of constant microscopic structure. With strict control of Mooney viscosity, percent ethylene, and percent ENB, so as to control the expected rheological properties and sulfuration velocity, greatly to decrease the unstability, which is serious for common EPDM. Using CGC and INSITE^{TM} technology, we could control the molecular chain branching and decrease the branching degree, which is important to the rubber processing. The polymer produced by the CGC technology had the narrow molecular weight distribution (MWD), but we could make the polymer have the perfect process properties and stable and uniform rheological behavior (see Table I), through the use of multilevel reactor so as to control the MWD especially, and thus solved the problems in processing.

POE Engage is another kind of polyolefin elastomer produced by the CGC technology, with density lower than 0.9 and hence called Super Low-Density PE (see Table II). It is a saturated copolymer of ethylene and octene, with a larger percentage of octene. In this compound, polyethylene crystalloid area acted as the physical crosslinked point, while the insertion of octene weakened the polyethylene crystallization, formed the amorphous area which had rubber elasticity, and the material transparence was good. By contrast with traditional polymer, POE has narrow MWD and short-branched chain ($\bar{M}_w/\bar{M}_n \approx 2$]), perfect physical and mechanical properties (high elasticity, high intensity, high elongation), good low temperature properties, and narrow MWD, making the material not to warp during the process of injection molding and extrusion; further the processing rheological

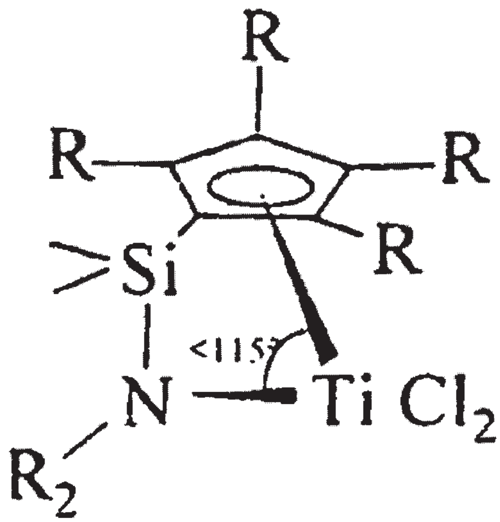

Figure 1 Sketch map of CGC activator structure.

properties can be improved by the insertion of the octene long-branch chain in the linear molecular chain, using the CGC technology.

The structure-principle of the double capillary rheometer of constant speed type

The rheological properties of new kind polyolefin elastomer were researched with the RH2000 double capillary rheometers (constant speed type) produced by the Bohlin Company, UK. The rheometer structure was showed in Figure 2. The left die was long ($L/D = 16$) and the right one was short ($L/D = 0.4$). The melt temperature in the both barrels were equal. Both the plungers were pushed down at the same speed, extruded the melt from both the dies. During the experiment the pressure values of P_L and P_R were measured from the two barrels. In fact, the pressure value P_R was equal to the entrance pressure drop. It reflected the melt elasticity; the difference of $P_L - P_R$ was equal to the pressure drop along the long die and it was used to calculate the viscosity. This design could do entrance pressure emendation easily, and need not to do Bagley emendation. The rheometer not only measured the melt viscosity and elasticity, but also measured the extension stress, extension viscosity, extrudate swell ratio, and evaluated the extrudate appearance.[4]

The measure temperature in this work:

EPDM nordel 3745p, 3722p: 150, 160, 170, 180°c;

POE Engage GPE 8003, 8150: 180, 190, 200, 210°C.

TABLE I
Physical Properties of EPDM Nordel IP

Physical properties (unit)	Nordel IP 3722P	Nordel IP 3745P
Mooney viscosity $ML_{1+4}{}^{121}$	22	45
Percent ethylene %	69	69
Percent propylene %	30.5	30.5
Percent ENB %	0.5	0.5
$\bar{M}_w$ (GPC)	100,000	150,000
MWD	Medium	Narrow
Density g cm^{-3}	0.88	0.88
Crystallinity (DSC) %	15	12
T_g °C	∼−50	∼−50

TABLE II
Physical Properties of POE Engage

Physical properties (unit)	GPE 8150	GPE 8003
Density (g cm^{-3})	0.87	0.89
Mooney viscosity $ML_{1+4}{}^{121}$	35	22
Percent Octene (%)	25	18
Melt index (g/10 min)	0.5	1.0
Melt point (DSC) (°C)	55	86
Tensile strength (MPa)	15.4	30.3
Ultimate elongation (%)	730	670
Hardness shore A	75	86
Flexural modulus (MPa)	16	40

RESULTS AND DISCUSSION

The comparision of apparent shear viscosity and non-newtonian fluidity

The apparent shear viscosity versus shear rate curves of the four samples at different temperatures were showed in the

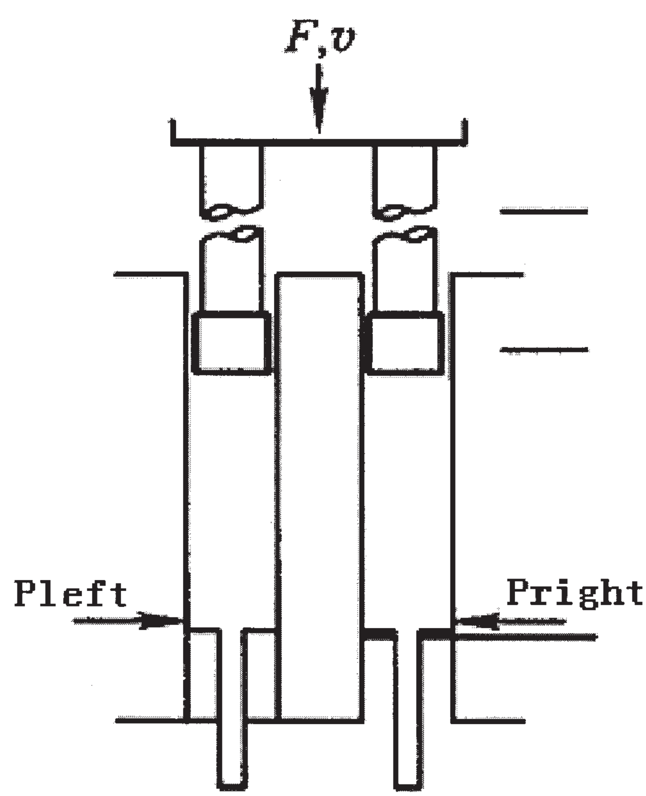

Figure 2 Sketch map of RH2000 Capillary rheometer.

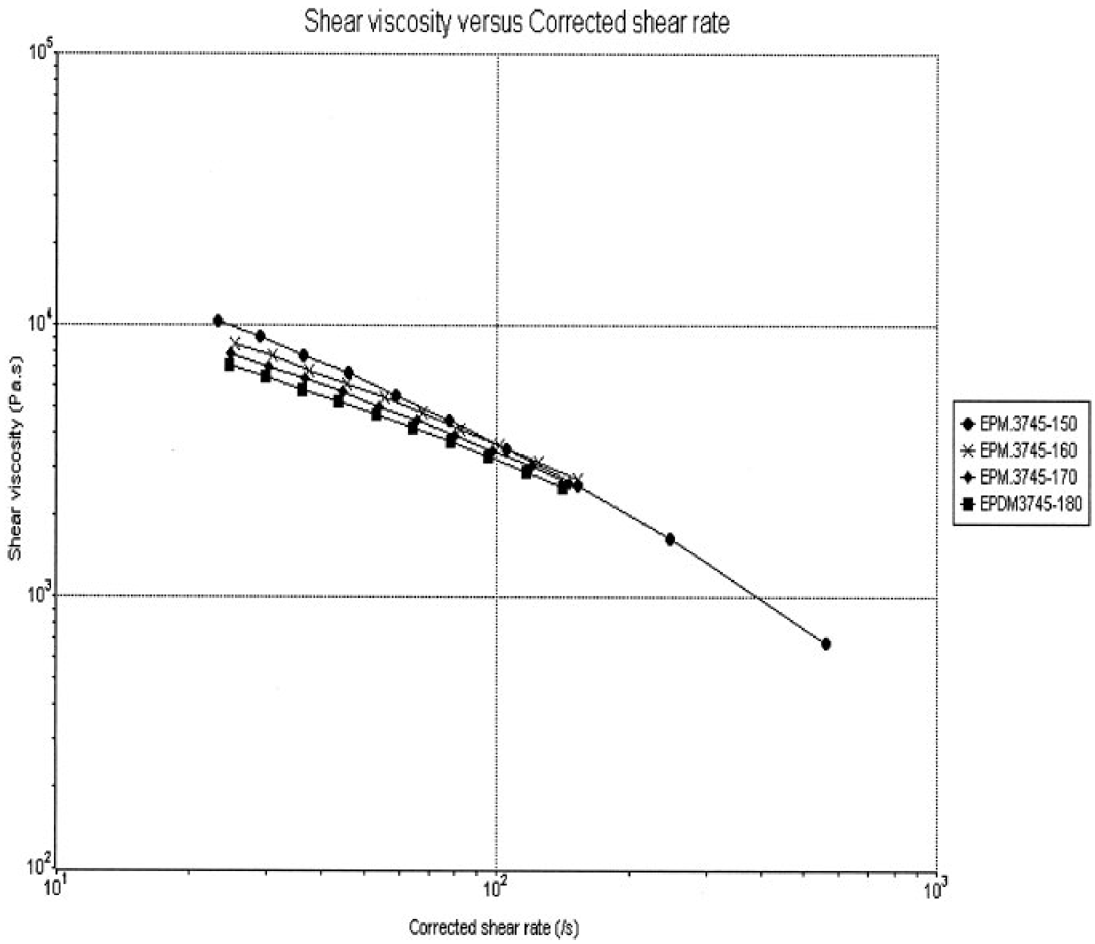

Figure 3 Viscosity curves of EPDM Nordel IP 3745P.

Figure 3–6. We could make the conclusion from these curves that the four samples were all pseudoplastic fluid, and the viscosity value would drop with the temperature rising. Compared with the EPDM Nordel3722P, the Nordel3745P had the larger molecular weight, higher Mooney viscosity, and the apparent shear viscosity (see Figs. 3 and 4). As regard to the non-Newtonian index (see Table III), the Nordel 3745P had lower *n* value, this means the nonlinear fluidity was high, which was related with its high molecular weight and narrow MWD.

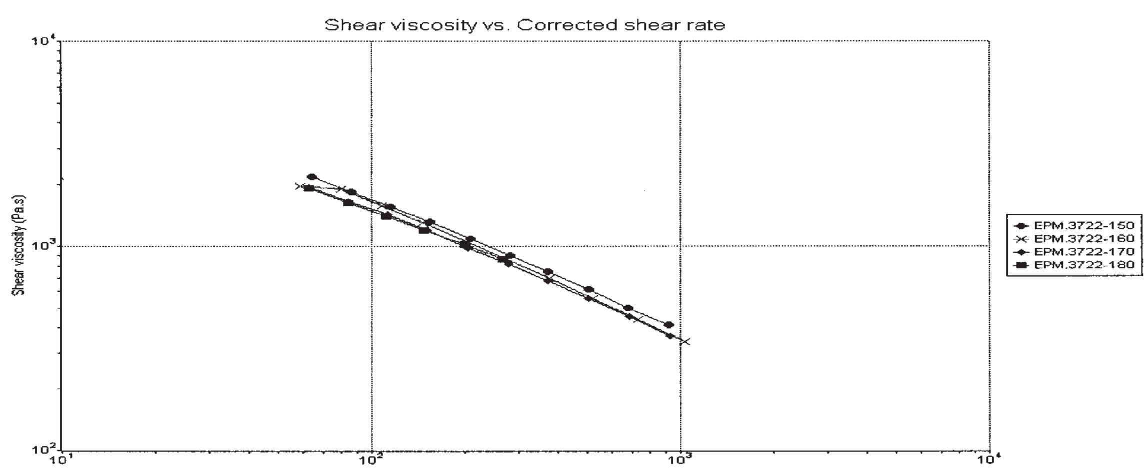

Figure 4 Viscosity curves of EPDM Nordel IP 3722P.

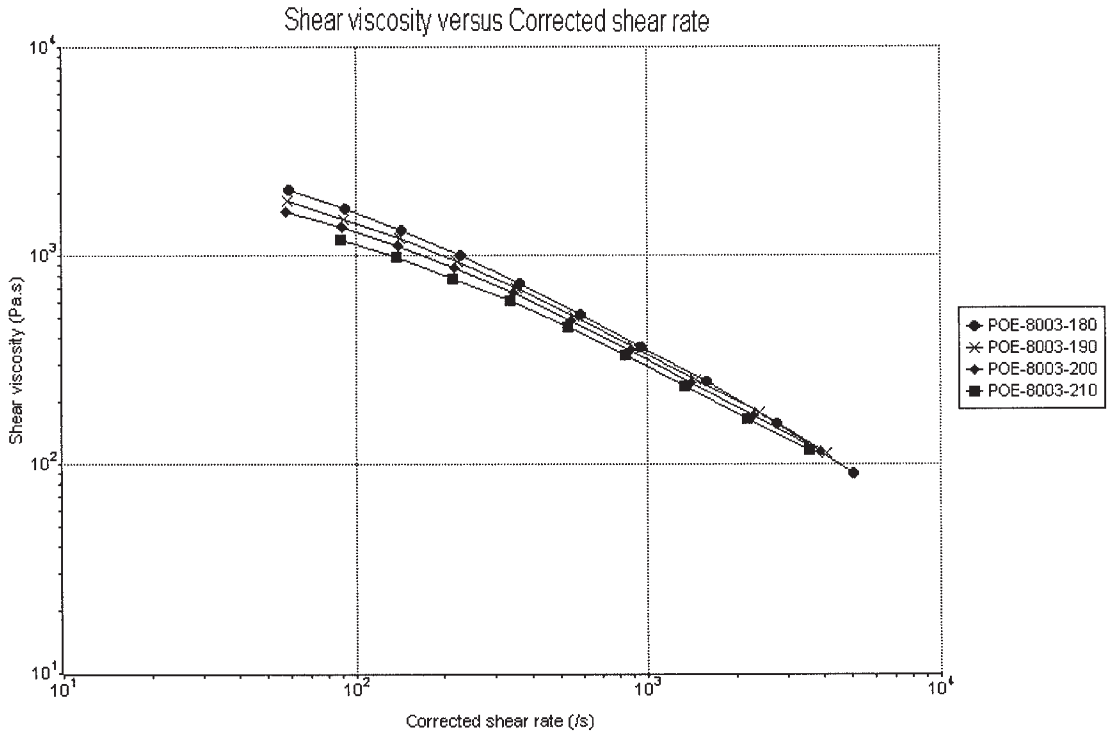

Figure 5 Viscosity curves of POE Engage GPE8003.

Compared between POE Engage GPE8003 and 8150(see Table II, Figs. 5 and 6), GPE8003 had the lower Mooney viscosity, larger melt index, lower molecular weight, but had the similar apparent shear viscosity with GPE8150, during the experiments. The differences between the both were listed as follows: (1)The viscosity of GPE8003 had more dependence on temperature, with the temperature rising, there were

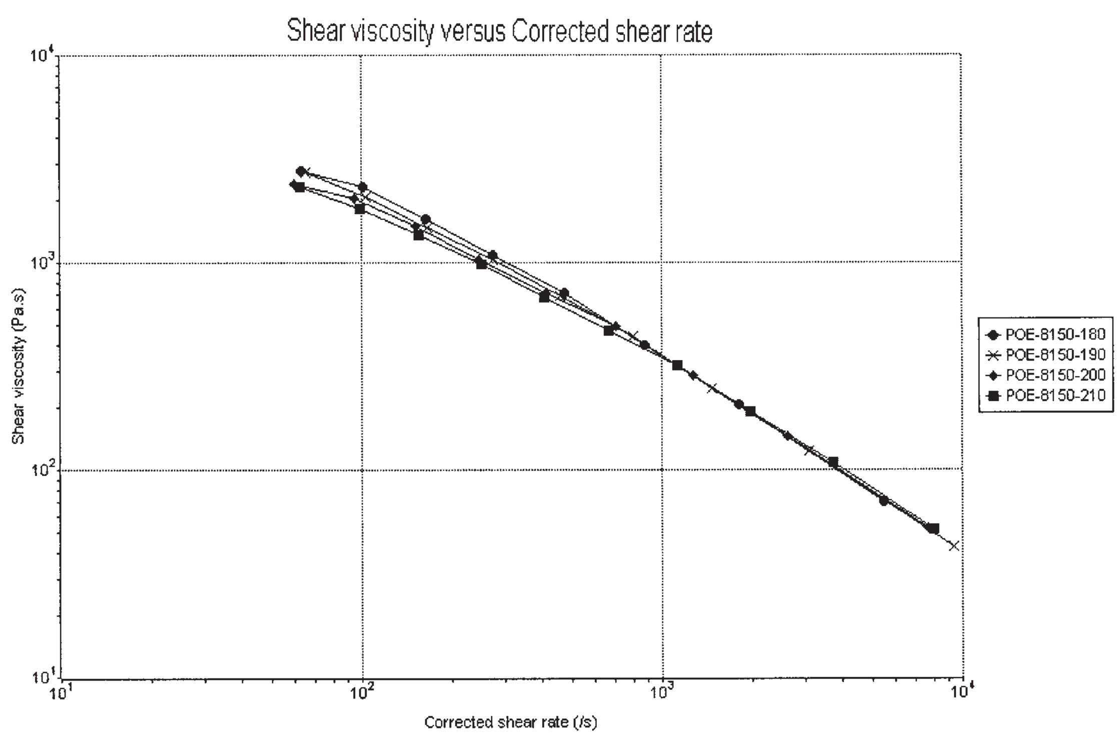

Figure 6 Viscosity curves of POE Engage GPE8150.

TABLE III
Non-Newtonian Index of Nordel IP 3745P and 3722P

Nordel IP 3745P		Nordel IP 3722P	
[dotγ] (s^{-1})	*n*	[dotγ] (s^{-1})	*n*
23.12	0.43	64.29	0.44
58.85	0.39	115.10	0.41
77.62	0.38	153.73	0.39
105.18	0.36	209.54	0.38
152.74	0.33	373.01	0.35
247.13	0.25	505.28	0.33
561.21	0.22	913.99	0.30

more drop in the viscosity. (2) The viscosity of GPE8150 had more dependence on shear rate, its non-Newtonian index was low (see Table IV), and the nonlinear fluidity was strong. This difference was related to the molecular structures. GPE8003 had lower octene percent, high crystallization and high density, so that the plasticity was more obvious. However the GPE8150 had the lower crystallization, its elasticity was obvious.

Extrudate swelling ratio, extrudate appearance, and melt fracture

The extrudate swelling ratio and extrudate appearance of the POE Engage GPE8003 and 8150 at different temperatures were shown in the Table V. It is observable that the extrudate appearance of GPE8003 was better than that of GPE8150, and the swelling ratio of extrudate of GPE8003 was smaller than that of 8150. This showed again that, because of the lower octene percent, GPE8003 had the higher crystallization, therefore more plasticity; while because of the higher octene percent, GPE8150 had lower crystallization, so that the density was low, and the elasticity was strong. The result showed again the relaxation of melt elasticity due to temperature. With the temperature rising, the extrudate appearance was improved, the critical shear rate at which the melt fracture occurred was increased, and the extrudate swelling ratio was reduced. The reason was that the relaxation time of the molecular chain movement was decreased with the increasing temperature and the melt elastic strain got more relaxation.

EPDM Nordel IP3745P and 3722P have the similar extrudate appearance. Table VI presents the swelling ratio of extrudate tested in long die ($L/D = 16/1$) and short die ($L/D = 0.4/1$) under different temperatures. From the Table, we can see the drop tendency of swelling ratio of extrudate with the increase in temperature. Comparing the two kinds of dies, we can see the swelling ratio of extrudate tested in long die is smaller than that in short die. This indicated that the elastic deformation of the melt experienced in the entrance of the die relax more in the long die. While in the short die, the elastic deformation do not have enough time to relax, so that the elastic reversion at the exit of the die is high. The pressure drop at the entrance of the short die reflected the melt elasticity (see Table VI) with regard to Nordel IP 3745P, the pressure drop at the entrance of the short die and the swelling ratio of extrudate at exit of the short die have good correspondence. With the melt temperature rising, the two decreased simultaneously. But with regard to Nordel IP3722P, the change tendency of the two was reverse. The swelling ratio of extrudate decreases with the increase in temperature, but in the meanwhile, the entrance pressure drop increases. The cause of that needs to be studied further.

The extrusion pressure vibration of EPDM Nordel IP 3745P

When EPDM Nordel IP3745P is extruded and when the volumetric flow is big enough, the melt desorption at the capillary wall and the "slip-stick transition" behavior were observed. The corresponding extrusion pressure vibrated regularly (see Fig. 7). The extent of pressure vibration was 3.50 MPa at long die, while at the short die was about 0.03 MPa, and the extrudate appeared regular bamboo-like.

From the standpoint of molecular structure, the "slip-stick transition" and pressure vibration phenomenon have some correlation with the lower branching of molecular chain, the higher molecular weight, and the narrow MWD. It is known that some linear molecular chain structure melt such as HDPE is apt to exhibit "slip-stick transition" behavior, and this phenomenon is apt to occur in the melt whose molecular chains had tight entanglement.[5] The Nordel IP 3745P produced by CGC technology has less-branched chain and it belong to linear molecular structure. It has high Mooney viscosity, high molecular weight, and narrow distribution of molecular weight (Table I). A large amount of its long molecular chains are easily entangled. All these resulted in pressure vibration easily.

From our former results, using the information of pressure vibration, we can calculate the slide velocity of melt at capillary wall and the corresponding extrap-

TABLE IV
Non-Newtonian Index of Engage GPE8003 and 8150

Engage GPE8003		Engage GPE8150	
[dotγ] (s^{-1})	*n*	[dotγ] (s^{-1})	*n*
57.85	0.56	59.84	0.46
89.57	0.52	94.61	0.41
139.01	0.48	151.06	0.36
218.45	0.43	246.17	0.30
345.71	0.39	411.12	0.25
1401.84	0.25	1275.60	0.13

TABLE V
Appearance and Swelling Ratio of Extrudate of Engage GPE8003 and 8150

	Engage GPE8003				Engage GPE8150			
	Appearance of extrudate				Appearance of extrudate			
[dotγ] (s^{-1})	180°C	190°C	200°C	210°C	180°C	190°C	200°C	210°C
50	A	A	A	A	B	B	A	B
75	A	A	A	A	B	B	B	B
113	B	B	A	A	D	C	C	B
171	C	B	B	A	D	D	D	C
260	C	C	B	B	E	D	D	D
390	C	C	C	B	F	F	D	D
586	D	D	C	C	F	F	F	E
883	E	D	D	C	F	F	F	F
1330	F	E	D	D	F	F	F	F
2000	F	F	E	E	F	F	F	F
Die swell ratio ([dotγ] =75 s^{-1})	1.30	1.28	1.22	1.16	1.40	1.38	1.36	1.32

A, smooth and transparent; B, sharkskin; C, fine thread; D, obvious thread; E, connected thread hill; F, separated thread.

TABLE VI
The Die Swell Ratio of Extrudate of Nordel IP 3745P and 3722P

Samples	Temperature (°C)	[dotγ] (s^{-1})	Die swell ratio: Long die L/D = 16	Die swell ratio: Zero die L/D = 0.4	Entry pressure at zero die (MPa)
Nordel IP 3745P	150	23.12	1.18	1.80	1.63
	160	25.28	1.16	1.78	1.56
	170	24.67	1.16	1.76	1.43
	180	24.54	1.14	1.74	1.34
Nordel IP 3722P	150	64.29	1.34	2.30	1.32
	160	58.92	1.32	2.28	1.45
	170	62.58	1.30	2.24	1.49
	180	62.92	Orange hull	Bamboo burl	1.84

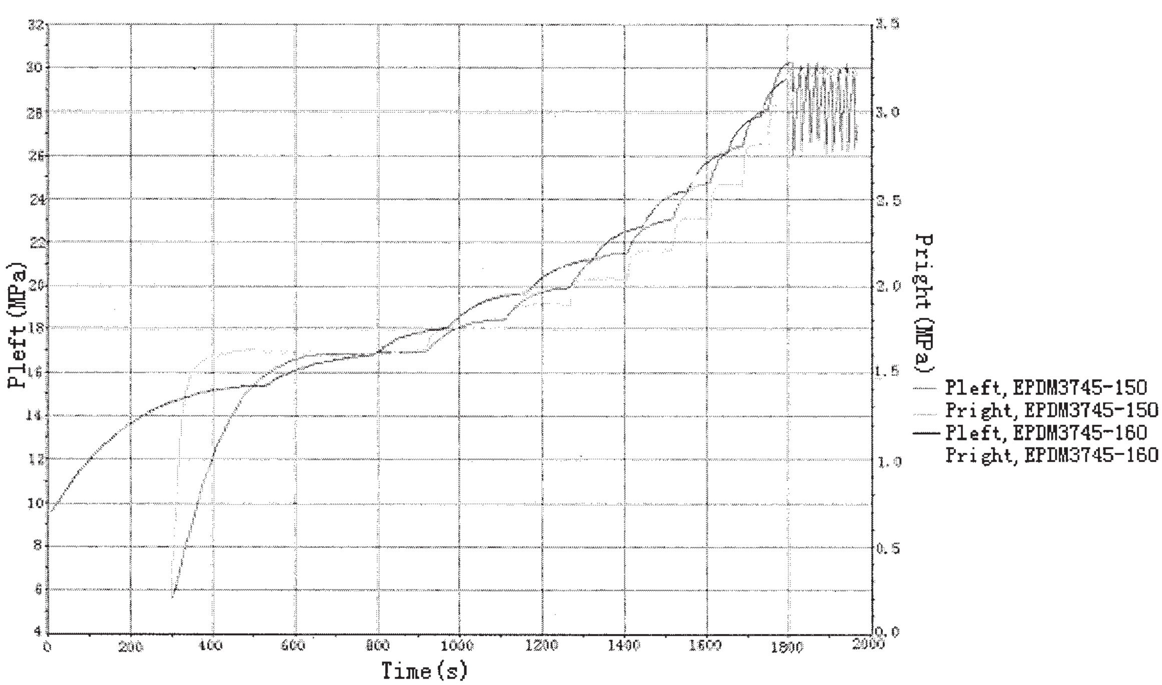

Figure 7 Pressure vibration of EPDM-Nordel3745P at 150°C.

TABLE VII
Slide velocity at Wall and Critical Slide Length of Nordel IP 3745P

Temperature (°C)	150
Pressure (MPa)	
Long die	
Maximum value of vibration	30
Minimum value of vibration	26.50
Zero die	
Maximum value of vibration	3.23
Minimum value of vibration	3.20
Slide velocity at wall v_s (mm sμ^{-1})	55.24
Critical slide length b_c (mm)	0.618
Amplitude of pressure vibration (MPa)	3.5
Period of pressure vibration (s)	20
Slide shear stress (MPa)	0.418

olation slide length b_c.[6] From Table VII, the slide velocity of Nordel IP 3745P was about several cm per second. Meanwhile, we can calculate the shear stress at wall.[7] When the melt began to slip, the critical shear stress corresponds to the absorption force between melt and capillary wall, and also to the maximum static friction force between melt and capillary wall. Compared with the critical shear stress of about 0.3 MPa of HDPE in documented report,[8] EPDM melt has a higher absorption force with metal wall (0.418 MPa), and it belong to high absorption melt with metal wall.

CONCLUSIONS

1. EPDM Nordel IP and POE Engage produced by CGC technology and INSITE™ technology are two kinds of polyolefin elastomer whose composition is very pure and has strict control on the structure and properties. The uniformity of the products is good. EPDM Nordel IP has a low branching density and, especially, the control of its MWD. It has good processibility and stable and uniform rheological properties. POE Engage has narrow MWD, and proper octene percent, and improved rheological properties.
2. The Comparison between EPDM Nordel IP 3745P and 3722P revealed that the first has higher viscosity and strong nonlinear fluidity. It is because of its high molecular weight and narrow MWD. When POE Engage GPE8003 and 8150 are compared, the viscosity of 8003 had more dependence on temperature, and the viscosity of 8150 had more dependence on shear rate, which was related to the octene percent in material.
3. When POE Engage 8003 and 8150 are compared, the extrudate appearance of former is better than that of the latter and the swelling ratio of extrudate of former is smaller. With the melt temperature rising, the appearance of extrudate became better, and the critical shear rate went up, while the swelling ratio went down.
4. When EPDM Nordel IP 3745P is extruded, the "slip-stick transition" behavior was observed and the extrusion pressure vibrated regularly. These are related to the low branching of molecular chain, the high molecular weight, the narrow MWD, and the more entanglement of molecular chain.

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