Ultrahigh Molecular Weight Ethene Copolymers from Metallocene and Ziegler Catalysts

*Koichi Hasebe,** *Akio Fujiwara, Takashi Nozaki, Koichi Miyamoto*

Summary: In this study, ultrahigh molecular weight polyethene homopolymer and copolymer were successfully produced with the metallocene and the Ziegler catalyst system. In case with the metallocene catalyst system, viscosity average molecular weight of the homopolymer was controlled from 2 million to 10 million. Also, the molecular weight of the copolymer was reached up to 6 million. In case with the Ziegler catalyst system, the molecular weight of the copolymer was reached up to 4 million. The transparency of the copolymer by the Ziegler catalyst, with which the copolymer with better uniformity was produced, could be comparable with that by the metallocene catalyst.

Keywords: metallocene catalyst; ultrahigh molecular weight ethene copolymer; Ziegler catalyst

Introduction

Ultrahigh molecular weight polyolefin, in particular ultrahigh molecular weight polyethene (UHMWPE) is excellent in impact resistance, abrasion resistance, sliding properties and chemical resistance compared to widely used polyethene, usable for sliding components, and has thus been ranked as one kind of engineering plastic.

UHMWPE with high crystallinity is white and opaque, and has poor transparency even if formed into thin sheet or film, impairing design properties of brand name as observed in the application for ski sole. In such actual situation, UHMWPE having excellent transparency is in demand. To improve transparency, an UHMWPE copolymer obtained from ethene and another α-olefin (comonomer) was proposed[1]. However, low polymerization temperature was necessary to produce the UHMWPE copolymer, by which the efficiency of the production was decreased. When the copolymerization was carried out at the practical temperature in the industrial process, which is from 70 °C to 100 °C, the molecular weight of the copolymer was too low to have the excellent abrasion resistance and friction coefficient, both of which were important characteristics of the UHMWPE.

On the other hand, it is well known that a highly active metallocene catalyst gives an ethene polymer, which has a narrow molecular weight distribution and a uniform distribution in the composition of constituent molecules. The problem in the polymerization process using the metallocene catalyst is that the polymerization rate is generally too high at initial stages to remove the heat of polymerization efficiently, and causes local heat generation spot in the obtained polymer. Thus, part of the polymer particles reaches the melting point or higher and fuses with each other to generate a bulk polymer. In a continuous process, generation of such bulk polymer results in clogging of polymer discharge tube of a polymerization reactor, making it impossible to remove the polymer, whereby continuous operation is disturbed.

Polyolefins Development Department, Polyethylene Division, Asahi Kasei Chemicals Corporation, 2767-11 Niihama, Shionasu, Kojima, Kurashiki, Okayama 711-8510, Japan
Fax: (+81)-86-458-3229;
E-mail: hasebe.kb@om.asahi-kasei.co.jp

Experimental Part

Catalyst and Treatments

All manipulations were carried out under a nitrogen atmosphere. All solvents were dehydrated with MS-13X before use. Tebbe reagent was synthesized from biscyclopentadienyltitanium dichloride and trimethylaluminium. A metallocene catalyst prepared from [(N-t-butylamide)(tetramethyl-η^5-cyclopentadienyl)-dimethylsilane]-titanium-1,3-pentadiene, bis(hydrogenated tallow alkyl)methylammonium-tris(pentafluorophenyl)(4-hydroxyphenyl)borate and silica treated with triethylaluminium was reacted with a small amount of hydrogen before use. Two types of Ziegler catalysts (Z-1 and Z-2) were used in this study. Z-1 catalyst was prepared with supporting technology from dibutylmagnesium, triethylaluminium, methylhydropolysiloxane, trichlorosilane, and titanium tetrachloride. Z-2 catalyst was prepared without supporting technology from dibutylmagnesium, triethylaluminium, methylhydropolysiloxane, and titanium tetrachloride.

Polymerization Procedure

Polymerization was carried out at 70 °C in a vessel-type reactor equipped with a stirrer. Solvent, ethene, the catalyst, and the Tebbe reagent were continuously fed to the reactor. The polymerization rate was 10 kg-PE/h.

Analytical Procedure

Viscosity average molecular weight (Mv) of polymers was calculated from the intrinsic viscosity ($[\eta]$) of the polymers according to the following formula.

$$\mathrm{Mv} = 5.34 \times 10^4 \times [\eta]^{1.49}$$

Density of polyethenes obtained was determined according to the method described in ASTM D1505. Measurement of haze of sheets produced with polyethenes was carried out according to the procedure described in ASTM D1003. Crystallinity of the polymer obtained was calculated from the heat of fusion measured by differential scanning calorimetry (DSC) with a DSC7 (PERKIN-ELMER Inc.). Molecular weight distributions (MWD) of polyethenes obtained were determined by gel permeation chromatography (GPC) with an alliance GPCV2000 (Waters Inc.) at 140 °C using *o*-dichlorobenzene as a solvent.

Results and Discussion

Ethene polymerization was conducted with the metallocene catalyst reacted with a small amount of hydrogen in order to prevent a generation of bulk polymer as well as to keep the polymerization activity high. The Tebbe reagent was continuously fed to the polymerization reactor in order to consume the hydrogen, which was also fed as a residue of the reaction with the catalyst, by the hydrogenation reaction of ethene, because Mv of the polymer immediately decreased by hydrogen, which was one of the strongest chain transfer reagent.

The results of ethene homo-polymerization were summarized in Table 1. The catalytic activity of the run No.1 was 5000g-PE/g-cat. Mv of the polymers increased from 2 million to 10 million as the feed rate of the Tebbe reagent to the reactor increased from 0.013 mmol/h to 0.38 mmol/h. Thus, it was found that molecular weight of UHMWPE could be controlled by the feed rate of the Tebbe reagent. No bulk polymer was produced, nor was the slurry discharge tube clogged, and consequently stable continuous operation was achieved.

Table 1.
Ethene homo-polymerization[a] with the metallocene catalyst.

Tebbe Reagent	Mv[b]	Density[c]	Crystallinity[d]
mmol/h	10^4	g/cm^3	%
0.013	210	0.930	51
0.038	440	0.928	48
0.13	920	0.927	46
0.38	1100	0.924	42

[a] Conditions: Solvent = 32 L/h, Cat. = 0.13 mmol/h, Production rate = 10 kg-PE/h;
[b] Mv was calculated from the intrinsic viscosity of the polymer obtained;
[c] Density was measured with ASTM-D1505;
[d] Crystalinity was calculated from the heat of fusion measured with DSC.

Table 2.
Co-polymerization[a] of ethene and 1-hexene with the metallocene catalst.

Tebbe Reagent	1-Hexene	Mv[b]	Density[c]	Crystallinity[d]	Haze[e]
mmol/h	L/h	10^4	g/cm^3	%	%
0.045	0.35	480	0.919	37	42
0.075	0.35	680	0.917	37	41
0.100	1.10	620	0.905	17	20
0.150	1.80	480	0.885	8	15

[a] Conditions: Solvent = 32 L/h, Cat. = 0.13 mmol/h, Production rate = 10 kg-PE/h
[b] Mv was calculated from the intrinsic viscosity of the polymer obtained
[c] Density was measured with ASTM-D1505
[d] Crystalinity was calculated from the heat of fusion measured with DSC
[e] Haze was measured with ASTM-D1003.

The results of ethene and 1-hexene co-polymerization were summarized in Table 2. UHMWPE copolymer was successfully synthesized by using the metallocene catalyst in the presence of the Tebbe reagent. The Mv values of the polymers obtained were about 5 million. The density and the crystallinity of the polymers decreased from 0.919 g/cm^3 and 37% to 0.885 g/cm^3 and 8%, respectively, as the feed rate of 1-hexene increased from 0.35 L/h to 1.80 L/h. The haze of the polymers deceased linearly as the density decreased. Thus, it is suggested that the haze of the polymers can be controlled by the feed rate of 1-hexene, same as a usual polyethene copolymer.

Ethene/1-butene copolymerization was conducted with the Ziegler catalysts (Z-1 and Z-2) and the results were listed in Table 3. UHMWPE copolymer was successfully synthesized by using the Z-1 catalyst. The Mv values of the copolymers obtained were controlled within the range of 2 million or more. The density of the copolymers decreased from 0.928 g/cm^3 to 0.917 g/cm^3, as the molar ratio of 1-butene to sum of ethene and 1-butene of the gas phase in the reactor increased from 2 mol% to 10 mol%. The production of the UHMWPE copolymer was occurred efficiently in industry, because the polymerization was carried out at 70 °C.

Figure 1 showed the relationship between the density and the haze of the UHMWPE copolymers synthesized in this study. The haze of the UHMWPE copolymer produced with the metallocene catalyst was lowest at the same density in all copolymers. The haze of the copolymer

Table 3.
Ethene and 1-butene copolymerization[a] with the Ziegler catalysts.

Cat.	1-butene[b]	Mv[c]	Density[d]	Hazd[e]
	mol%	10^4	g/cm^3	%
Z-1	0	500	0.928	82
Z-1	2	350	0.922	69
Z-1	5	300	0.919	53
Z-1	10	240	0.917	46
Z-2	5	170	0.920	71
Z-2	10	120	0.920	70

[a] Conditions: Solvent = 65 L/h, Production rate = 6 kg-PE/h;
[b] Molar ratio of 1-butene to sum of ethene and 1-butene;
[c] Mv was calculated from the intrinsic viscosity of the polymer obtained.
[d] Density was measured with ASTM-D1505.
[e] Haze was measured with ASTM-D1003.

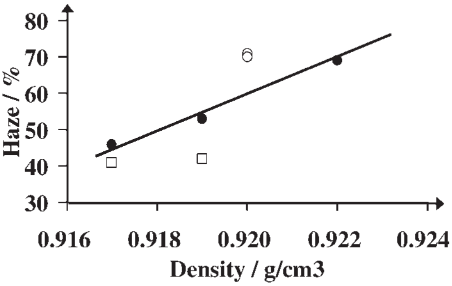

Figure 1.
Relationship between the density and the haze of the UHMWPE copolymers produced with various catalysts; ●: Z-1 catalyst, ○: Z-2 catalyst, □: metallocene catalyst.

produced with the Z-1 catalyst was much better than that with the Z-2 catalyst, and was comparable with that by the metallocene catalyst.

It was very difficult to measure the molecular weight distribution and comonomer content of the UHMWPE copolymer, because the molecular weight of the copolymers was too high to be solved to almost any solvent. Thus, the polyethene copolymers having usual molecular weight were prepared with both the Z-1 and the Z-2 catalyst in order to presume the structure of the UHMWPE copolymers from that of the copolymers.

From the NMR analysis of the copolymers, comonomer content of the copolymer produced with the Z-1 catalyst was less than that with the Z-2 catalyst. The density of the copolymers was almost the same. Thus, comonomer distribution was much more uniformly produced with the Z-1 catalyst than that with the Z-2 catalyst. From the GPC analysis, MWD of the copolymer produced with the Z-1 catalyst was narrower than that with the Z-2 catalyst. Thus, it was suggested that the UHMWPE copolymer produced with the Z-1 catalyst was more uniform, that is narrower MWD and narrower comonomer distribution, than that with the Z-2 catalyst.

Based on the above analyses of the copolymers, it was considered that the more uniform both the MWD and the comonomer distribution of the UHMWPE copolymer were, the more uniform both the thickness of the lamella and the size of the spherical crystal were, because the uniformity was not disturbed the optical transmission through the UHMWPE copolymer. Thus, the transparency of the UHMWPE copolymer produced with the catalyst, by which the relatively uniform copolymer was produced, was better.

Conclusion

The UHMWPE copolymer was successfully produced with the metallocene catalyst and the Tebbe reagent. The molecular weight of the copolymer produced with the metallocene catalyst was reached up to 6 million by increasing the concentration of the Tebbe reagent. The haze of the copolymer was remarkably improved by decreasing the density. The UHMWPE copolymer was efficiently produced with the Ziegler catalyst, too. The copolymer by the Z-1 catalyst, with which the copolymer with better uniformity was produced, had higher molecular weight and better transparency than that by the Z-2 catalyst, with which the copolymer with worse uniformity was produced. The transparency of the copolymer produced with the Z-1 catalyst was comparable with that with the metallocene catalyst.

[1] T. Hayashi, T. Shiraki, A. Kato, JP-B-05-86803.