Thermal and mechanical properties of ethylene/α-olefin copolymers produced over (2-MeInd)₂ZrCl₂/MAO system

J.-S. Yoon[a,*], D.-H. Lee[a], E.-S. Park[a], I.-M. Lee[b], D.-K. Park[b], S.-O. Jung[b]

[a]*Department of Polymer Science and Engineering, Inha University, 402-751 Inchon, South Korea*
[b]*Department of Chemistry, Inha University, 402-751 Inchon, South Korea*

Abstract

Thermal and mechanical properties of ethylene/α-olefin copolymers (LLDPE) produced over bis(2-methyl indenyl)zirconium dichloride((2-MeInd)₂ZrCl₂) were compared with those of LLDPEs synthesized with a conventional heterogeneous Ziegler–Natta (Z–N) catalyst, titanium tetrachloride supported on magnesium diethoxide with diisobutyl phthalate as an internal donor(Mg(OEt)₂/DIBP/TiCl₄). DSC thermogram of LLDPE by the Z–N catalyst showed that the melting peak moved to a lower temperature region and the peak became broader as the density of LLDPE decreased. On the other hand, in case of LLDPE produced over (2-MeInd)₂ZrCl₂, the melting peak shifted to a lower temperature zone with the decreasing copolymer density without a significant loss in the peak sharpness. The density of LLDPE was a decreasing function of mole fraction of α-olefin, and the decrease was more pronounced as the molecular weight of the incorporated α-olefin increased. However, when the density was plotted against weight fraction of α-olefin, a similar declining curve was observed irrespective of the type of α-olefins except the LLDPE made by the Z–N catalyst in which more α-olefin units were required to reach the same density as that of LLDPEs by (2-MeInd)₂ZrCl₂. LLDPE made by the Z–N catalyst had lower tensile strength but similar elongation and elastic modulus compared to those of poly(ethylene-*co*-1-dodecene) and poly(ethylene-*co*-1-octadecene) synthesized by (2-MeInd)₂ZrCl₂. Poly(ethylene-*co*-1-hexene) by (2-MeInd)₂ZrCl₂, however, exhibited lower elastic modulus and higher elongation compared with the other LLDPEs. Measurement of dynamic mechanical properties of LLDPEs revealed that β-transition peak appeared at a lower temperature and became more intense, as the density decreased, until the crystallinity of LLDPEs disappeared completely when the β-transition peak became fixed around −45°C. γ-transition was monitored at around −125°C and was thought to be induced by the limited motion of the main backbone chain. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Metallocene catalyst; Ziegler–Natta catalyst; Copolymerization

1. Introduction

The reactivity of the conventional heterogeneous Ziegler–Natta (Z–N) catalysts towards ethylene is much higher than that toward α-olefins [1–6]. Owing to these characteristics it is not easy to copolymerize ethylene with α-olefins larger than 1-octene to prepare ethylene/α-olefin copolymers (LLDPEs) containing long chain branches. Heterogeneity of active sites in the Z–N catalysts caused the formation of the copolymer with broad polydispersity and comonomer composition distribution. In the copolymers from the Z–N catalyst, a lower molecular weight fraction has a higher content of α-olefin units, and a higher molecular weight fraction has a lower α-olefin units, which broadens the melting temperature spectrum, increases extractables and smell, and thus limits

applicability and processability of the copolymers [7–10]. Contrary to low density polyethylene (LDPE) which contains short chain branches as well as long chain ones, LLDPE produced by the metallocene catalysts can be endowed only with long chain branches because metallocene catalysts could be designed to show a high reactivity towards long chain α-olefins as well as towards ethylene. The metallocene LLDPE has polydispersity and composition distribution much narrower than LDPE or the Z–N LLDPE. The narrower polydispersity and composition distribution allow the metallocene LLDPE to have better transparency, fewer local weak points and level of tension stiffening equivalent to that of LDPE. The tension-stiffening behavior in elongational viscosity comes from the fact that the chain branches anchor the chain motion. In terms of viscosity branched polymers have lower zero-shear viscosity than linear homologues of the same total molecular weight when the branches are shorter than those needed for chain entanglement ($M_b < M_e$). When $M_b > M_e$, the

Table 1
Characteristics of LLDPE

Code	Comonomer type	M_w ($\times 10^5$)	M_w/M_n	T_m (°C)	X_c (%)	Density (g/cm^3)	E modulus (GPa)	Yield stress (MPa)	Maximum stress (MPa)	Elongation at break (%)	β-transition peak temperature (°C)	β-transition peak strength
HDPE 939	–	7.06	3.07	135.0	55.0	0.939	0.74	25.96	33.99	1019.8	–	–
MH 923	1-Hexene	25.78	2.29	116.5	35.4	0.923	0.21	13.13	31.29	865.5	–	–
MH 918	1-Hexene	23.23	2.54	111.3	29.8	0.918	0.15	10.98	29.65	886.0	−8	0.067
MH 912	1-Hexene	25.66	2.71	104.1	22.4	0.912	0.099	9.41	31.45	879.9	−10	0.082
MH 905	1-Hexene	23.01	2.63	86.5	13.7	0.905	0.098	7.12	34.07	822.3	−18	0.103
MH 894	1-Hexene	3.05	3.66	–	22	0.894	0.062	–	37.67	954.5	−38	0.262
MH 879	1-Hexene	2.17	2.72	–	–	0.879	0.043	–	29.97	936.2	−40	0.32
MH874	1-Hexene	2.25	2.89	–	–	0.874	0.039	–	26.01	943.5	−36	0.338
MD 918	1-Dodecene	46.71	2.31	118.5	29.3	0.918	0.32	–	31.06	731.6	−16	0.07
MD 916	1-Dodecene	48.23	2.32	113.0	26.4	0.916	0.24	–	37.22	788.5	−14	0.082
MD 913	1-Dodecene	12.33	1.78	109.3	23.4	0.913	0.23	–	32.66	776.3	−10	0.096
MD 911	1-Dodecene	12.55	1.78	105.2	21.0	0.911	0.18	–	32.44	753.2	22	0.104
MD 910	1-Dodecene	18.76	2.72	104.8	19.9	0.910	0.14	–	29.97	807.1	−26	0.104
MD 907	1-Dodecene	3.72	2.28	98.8	17.6	0.907	0.11	–	25.67	781.0	−28	0.111
MO 919	1-Octadecene	24.16	3.02	118.0	30.3	0.919	0.34	–	41.54	745.5	−10	0.067
MO 915	1-Octadecene	24.61	2.76	111.3	25.3	0.915	0.25	–	43.10	705.2	−14	0.082
MO 912	1-Octadecene	23.33	2.57	101.1	22.8	0.912	0.20	–	43.94	784.1	−14	0.101
MO 904	1-Octadecene	20.18	2.58	98.8	15.0	0.904	0.18	–	38.39	797.6	−16	0.125
ZH 924	1-Hexene	2.43	4.09	122.9	36.2	0.924	0.50	14.19	25.16	832.5	–	–
ZO 919	1-Octene	3.24	4.39	122.3	32.0	0.919	0.31	10.02	22.53	806.0	−18	0.07
ZH 918	1-Hexene	2.96	4.40	122.1	28.1	0.918	0.31	9.65	17.48	815.3	−20	0.06
ZB 900	1-Butene	3.91	4.38	–	7.4	0.900	0.12	–	15.77	797.3	−22	0.101
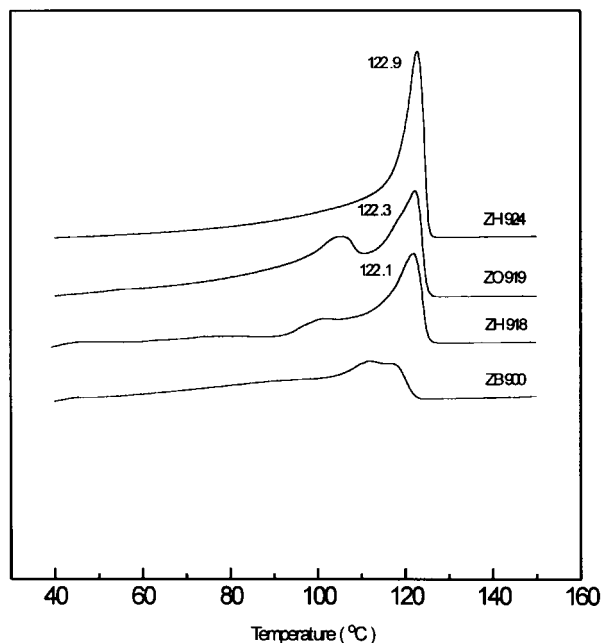
Fig. 1. DSC thermograms of LLDPEs produced over a Ziegler–Natta catalyst (Mg(OEt)$_2$/DIBP/TiCl$_4$–TEA).

branched chain viscosities overtake those of the equally massive linear chains [11].

Polyolefins with narrow molecular weight distribution generally exhibit poor processibility, but INSITE® resin from Dow's CGCT(constrained geometry catalyst technology), where ethylene and 1-octene are copolymerized, was claimed to show high pseudoplasticity and good processibility despite their narrow polydispersity [9,12–15].

When the relationship between structure and properties of LLDPEs is established, it is expected to be possible to design the metallocene catalyst structure and comonomer type to produce LLDPEs possessing specific desired properties [12–20].

In this study, LLDPEs were prepared with the unbridged metallocene catalyst (2-MeInd)$_2$ZrCl$_2$, which showed a high reactivity toward long-chain α-olefins. (2-MeInd)$_2$ZrCl$_2$ produced polypropylene(PP) with [mm] triad fraction of 0.33 and [mr] triad fraction of 0.47 at −20°C, indicating that the exchange rate between racemic state and meso state of the catalyst was so fast that the PP was almost atactic [21]. Therefore (2-MeInd)$_2$ZrCl$_2$ can be thought to be a single site catalyst, and synthesize LLDPEs with narrow composition distribution, even though the catalyst activity in racemic state is different from that in meso state.

Chain length of the side branches in LLDPEs was varied by copolymerizing ethylene with α-olefins of different chain length. The copolymer composition distribution was estimated by measuring the melting peak broadness, and the depression in the melting temperature and density according to the content of α-olefins.

Thermal and mechanical properties of the copolymers were investigated using UTM, Rheovibron and DSC, and compared to those of LLDPEs produced with the conventional heterogeneous Z–N catalysts.

2. Experimental

Copolymers of ethylene/1-hexene, ethylene/1-dodecene and ethylene/1-octadecene were synthesized using (2-MeInd)$_2$ZrCl$_2$/MAO catalyst.

All polymerization reactions were carried out in a 500 ml glass reactor with a magnetic stirrer. 100 ml of toluene was employed as the reaction medium and the reaction temperature was 0°C. Ethylene gas was first introduced at 1 atm and α-olefin was added using a syringe. The polymerization was initiated by addition of MAO and (2-MeInd)$_2$ZrCl$_2$. Al/Zr ratio was maintained at 2000. The reaction time was 30 min and the reaction was terminated by adding a mixed solution of methanol and HCl. The products were washed three times with plenty of methanol and dried in a vacuum oven (30°C) until constant weight was attained. Ethylene/1-butene, ethylene/1-hexene and ethylene/1-octene copolymers were prepared with Mg(OEt)$_2$/DIBP/TiCl$_4$–TEA (provided by the physical milling method by Korea Petrochemical Co.) for the purpose of comparison. Triethylaluminum (TEA) and Mg(OEt)$_2$/DIBP/TiCl$_4$ were added to the reaction medium in this order. Polymerization was carried out at 70°C for 1 h with Al/Ti mole ratio of 150.

Table 1 summarizes the characteristics of the LLDPEs obtained. Densities of the copolymers were measured by a density gradient column prepared using isopropanol and distilled water. Calibration was achieved using LLDPEs of known density. Each density was measured four times and the average was taken. Composition of α-olefin units was determined from NMR spectra recorded at 130°C on a Bruker AC-250 FT–NMR spectrometer. 20–50 mg of the polymers was dissolved in 0.3 ml of 1,2,4-trichlorobenzene(10 wt% of 1,2 dichlorobenzene-d$_4$ mixed solvent) and was subjected to the NMR measurements. Molecular weight and molecular weight distribution were measured using GPC (Waters 150C plus with a differential refractometer detector and a column composed of Styragel® HT6E, HT5 and HT3) with 1,2,4-trichlorobenzene (1.0 ml/min) as an eluent at 135°C using polystyrene(Showadenko SL-105) as a standard. Thermal properties of the polymers were obtained using DSC (Perkin Elmer DSC 7). The DSC thermogram was obtained for 7 mg of the sample sheet by scanning from room temperature to 160°C at a rate of 10°C/min. Crystallinity was represented as the ratio of melting enthalpy of the DSC thermogram to that of a perfect polyethylene crystal(290 J/g) [16]. The stress–strain behaviors were measured for specimens (40 mm × 10 mm × 0.2 mm^t) according to ASTM D 882(thin plastic sheeting) using an universal testing machine(UTM, model H25K-S, Hounsfield Co.). The distance between the grips was 20.0 mm and the test rate was set at 50 mm/min. The dynamic mechanical properties were measured with Rheovibron
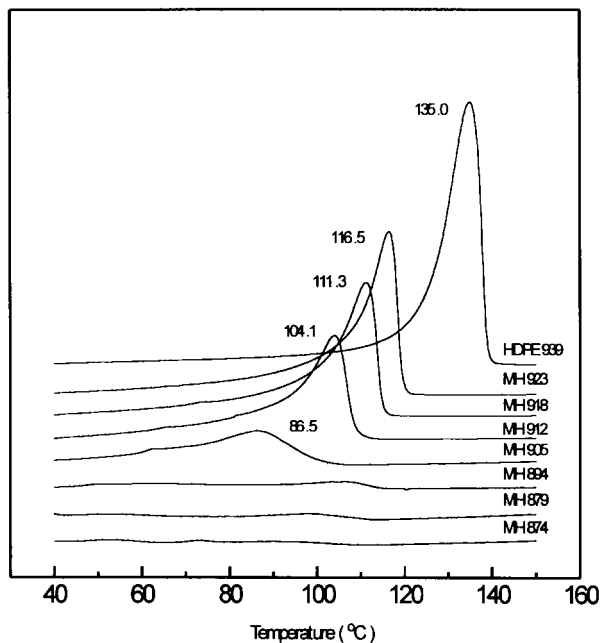
Fig. 2. DSC thermograms of poly(ethylene-*co*-1-hexene) produced over (2-MeInd)$_2$ZrCl$_2$/MAO.

(DDVII, Toyo Baldwin Co.). The dimension of the sample was 40 mm × 5 mm × 0.2 mm^t and the properties were measured in the range between −150 and 100°C at the frequency of 3.5 and amplitude factor of 30.

Specimens were prepared by pressing the polymerized powder on a hot press at 170°C under 275 psi for 5 min and subsequently under 690 psi for 1 min and finally quenching into ice water.
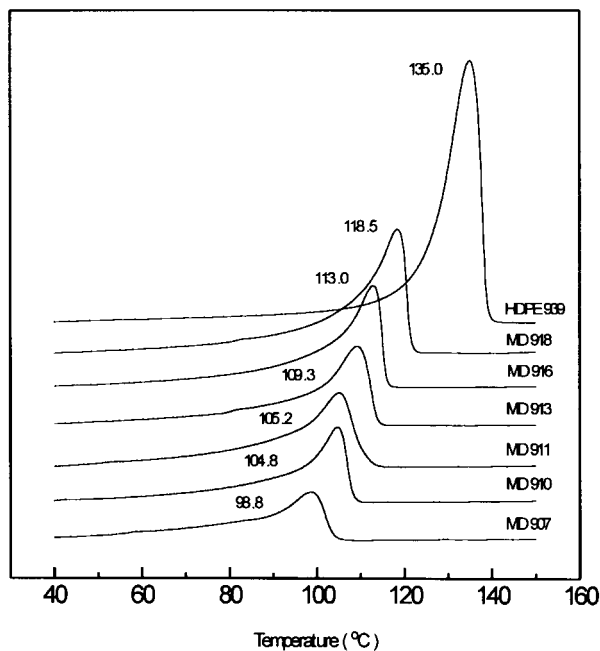

Fig. 3. DSC thermograms of poly(ethylene-*co*-1-dodecene) produced over (2-MeInd)$_2$ZrCl$_2$/MAO.
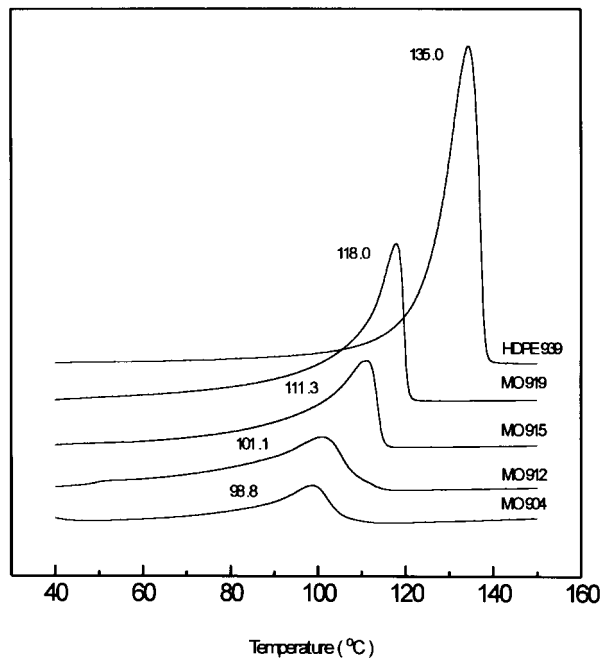
Fig. 4. DSC thermograms of poly(ethylene-*co*-1-octadecene) produced over (2-MeInd)$_2$ZrCl$_2$/MAO.

3. Results and discussion

3.1. Melting behavior

Fig. 1 shows a DSC thermogram of LLDPE prepared with the Z–N catalyst. Z represents that samples were prepared by the Z–N catalyst. H, O and B represent that 1-hexene, 1-octene and 1-butene were copolymerized, respectively, with ethylene. The numbers on the sample code correspond to the density of copolymers in kg/m^3. Melting point and heat of fusion tended to decrease as the density of the copolymer decreased. The copolymer with lower density started to melt at a lower temperature, but the upper bound of the melting peak was nearly fixed at 120°C irrespective of the copolymer density. It is to be noted that ZO 919, a copolymer of ethylene and 1-octene whose density is 0.919 g/cm^3, showed a much broader bimodal melting peak than ZH 918, a copolymer of ethylene and 1-hexene, indicating the former LLDPE had broader composition distribution than the latter. The broadening of melting peaks could be attributed to the coexistence of low molar mass highly branched copolymer molecules with high molar mass copolymer molecules containing a lower content of α-olefin units [2,22–28]. Figs. 2–4 show, respectively, DSC thermograms of copolymers of ethylene/1-hexene, ethylene/1-dodecene and ethylene/1-octadecene, synthesized using (2-MeInd)$_2$ZrCl$_2$. In the case of poly(ethylene-*co*-1-hexene), the melting peak shifted to lower temperature region without a significant broadening of the melting peak as the copolymer density decreased. The decrease of the melting point of LLDPEs by (2-MeInd)$_2$ZrCl$_2$ could be, at least in
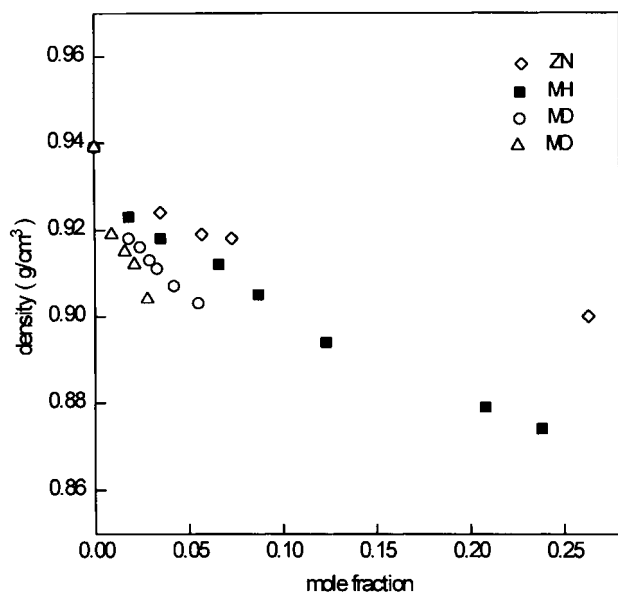
Fig. 5. Plot of comonomer mole fraction vs. density of LLDPEs.

part, ascribed to the lower molecular weight of LLDPEs containing higher content of α-olefin units. However an empirical equation for melting point of polyethylenes as a function of molecular weight has been given by Wunderlich [29] as $T_m = (414.1–2071)/(\text{number of carbons})$. Hence it can be said that the molecular weight of LLDPEs in Table 1 are high enough for the melting point to be in the plateau region.

Figs. 3 and 4 demonstrate that copolymers with narrow composition distribution were formed by (2-MeInd)$_2$ZrCl$_2$, in view of the fact that the melting peak remained sharp even though large sized α-olefins such as 1-dodecene or 1-octadecene were copolymerized with ethylene, as

Fig. 6. Plot of comonomer weight fraction vs. density LLDPEs.

compared with the broad melting peak of LLDPEs from the Z–N catalyst.

Fig. 5 shows the dependence of the density of LLDPEs on the α-olefin content. As the chain length of the α-olefin increases, the density of LLDPEs as a function of mole fraction of the α-olefin decreases more rapidly. However, as shown in Fig. 6, when the density was plotted against weight fraction of the α-olefin, the density of LLDPE by (2-MeInd)$_2$ZrCl$_2$ declined following almost identical curve regardless of the types of the α-olefins.

It is generally accepted that the crystallinity, and thus the density, of polyethylenes depend strongly on the short chain branches. As for the long chain branches, they have little effects on the crystallinity, as far as the long chain branches are long enough to be co-crystallized with the main backbone chains, though the rate of crystallization may be affected [30]. The more pronounced effect of 1-octadecene units on the copolymer density, compared to that of 1-hexene or 1-dodecene units, indicates that the 16-carbon side chain branches are not long enough to co-crystallize effectively. For isotactic polypropylene, the minimum number of isotactic units in a sequence required for crystallization of polypropylene was determined to be 14, i.e. 28 carbons, from transmission electron microscopy observations [31].

Since the plot of the copolymer density vs. weight fraction of branching units followed almost identical curves irrespective of the type of α-olefins, it can be said that the decrease of density of metallocene LLDPEs is almost proportional to the number of carbons in the α-olefin units, unless the side chains co-crystallize spontaneously.

The density of the Z–N LLDPEs declined more slowly and required more α-olefins units to attain the same density values as that of LLDPEs produced by (2-MeInd)$_2$ZrCl$_2$. This was ascribed to the fact that the high molecular weight fraction in the Z–N LLDPEs, which constituted the bulk of the crystalline phase, was not as much branched as that in the LLDPEs from (2-MeInd)$_2$ZrCl$_2$.

3.2. Stress–strain behavior

Extensive studies have been done on the stress–strain behavior of polyolefins [32–38]. Table 1 summarizes elastic modulus, yield stress, maximum stress and elongation at break of LLDPEs produced by (2-MeInd)$_2$ZrCl$_2$ and by the Z–N catalyst. The data were taken as average of at least five measurements and the standard deviation is shown as an error bar in Figs. 7–9. Elastic modulus decreased more rapidly than maximum stress or elongation as the α-olefin content increased. As polymer molecular weight increases, the sum of the attractive forces between adjacent polymer molecules increases correspondingly, and eventually the sum of the attractive forces exceeds the strength of the primary covalent bonds within the individual molecules. Further increase in molecular weight does not contribute any more to the mechanical properties. Thus
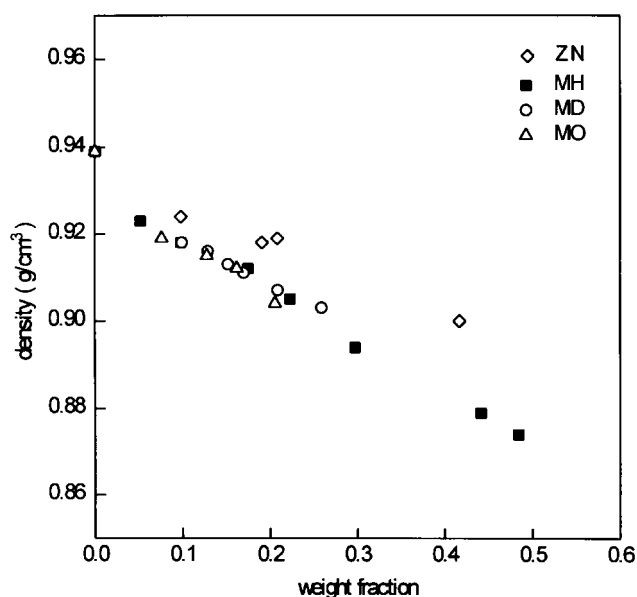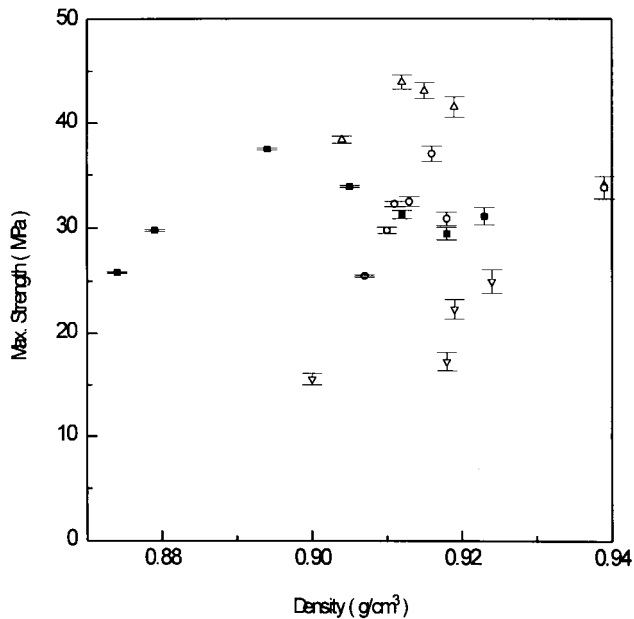
Fig. 7. Maximum strength as a function of density of LLDPE: ▽ ZN; ■ MH; ○ MD; and △ MO.

Fig. 9. Elastic modulus as a function of density of LLDPE: ▽ ZN; ■ MH; ○ MD; and △ MO.

tensile strength, elongation and other stress–strain properties are correlated with the degree of polymerization (DP) as $a - (b/DP)$, and increase rapidly with DP to level off at DP of 600–700 [39]. LLDPEs in Table 1 have molecular weight well above 1.0×10^5. Therefore it can be said that the difference in the molecular weight of the LLDPEs was not the main cause for the discrepancy of the mechanical properties.

Maximum strength of the Z–N LLDPE was lower than that of LLDPE by (2-MeInd)$_2$ZrCl$_2$. However elastic moduli

and elongation of the Z–N LLDPE were almost identical with those of the other LLDPEs.

Elastic modulus of LLDPEs decreased with decrease of the density in the same manner regardless of the length of chain branches except that MH was softer than the other LLDPEs. The higher elastic modulus and the lower elongation of MD(poly(ethylene-co-1-dodecene)) or MO(poly (ethylene-co-1-octadecene)) in comparison with those corresponding to MH(poly(ethylene-co-1-hexene)) should be, in part, ascribed to the presence of long chain branches

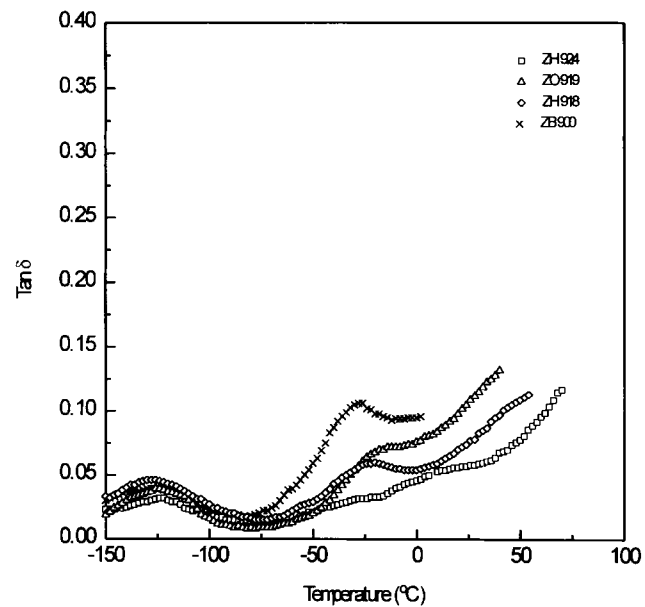Fig. 8. Elongation at break as a function of density of LLDPE: ▽ ZN; ■ MH; ○ MD; and △ MO.

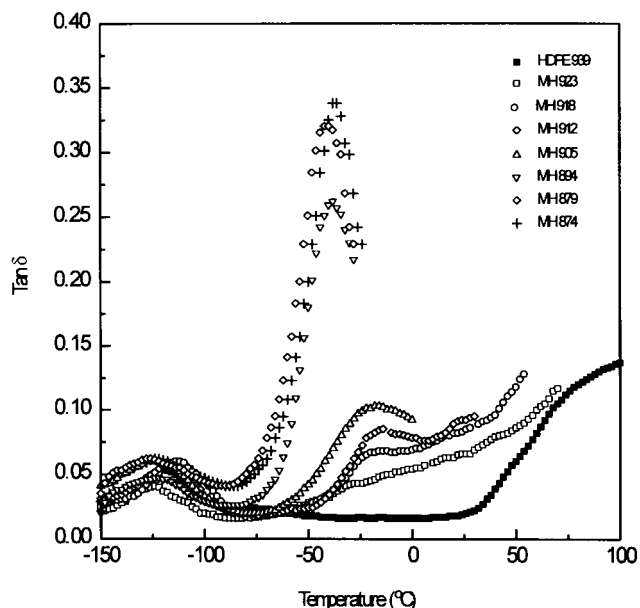Fig. 10. Tan δ curves of LLDPEs produced over heterogeneous Ziegler–Natta catalysts.

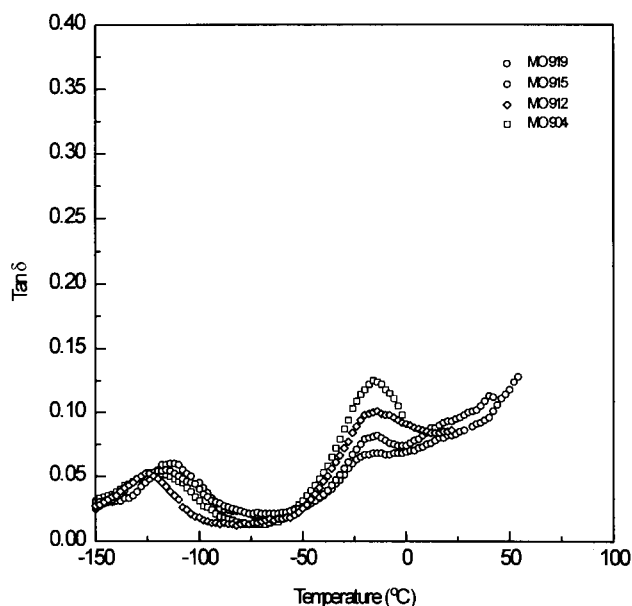Fig. 11. Tan δ curves of metallocene LLDPEs(ethylene/1-hexene copolymer).

Fig. 13. Tan δ curves of metallocene LLDPEs(ethylene/1-octadecene copolymer).

in MD or MO, which could serve as anchors during the stress–strain experiments. In contrast, Sehanobish et al. [40] reported that the elastic modulus of aliphatic chain branched LLDPE of similar crystallinity was nearly independent of branch length and branching distribution. Meanwhile, they observed significant enhancement of elastic modulus as the aliphatic branches were replaced with cyclic branches such as in the poly(ethylene-*co*-norbornene) copolymers.

More data are needed to draw a clear conclusion on the dependence of the mechanical properties upon the molecular structure of LLDPEs.

3.3. Dynamic mechanical behavior

In Figs. 10–14, relationships between tan δ and temperature were plotted for the four types of LLDPEs. Intensity of β-transition peak increased and the peak shifted to a lower temperature zone with decrease in the copolymer density. However, as the density of LLDPE decreased further, so that the crystalline phase of LLDPE disappeared almost completely, the β-transition peak became fixed at around $-45°C$ (Fig. 11). β-transition of the semicrystalline polymers has been reported to be dependent on crystallinity as
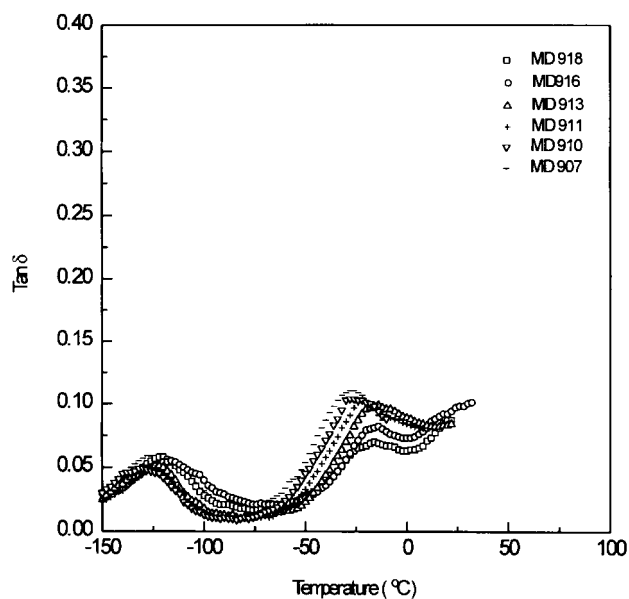

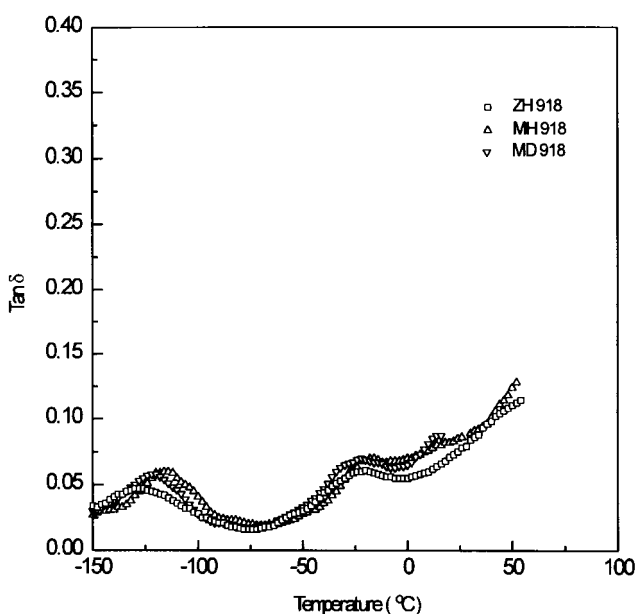Fig. 12. Tan δ curves of metallocene LLDPEs(ethylene/1-dodecene copolymer).

Fig. 14. Tan δ curves of LLDPEs of similar density.

well as on T_g [26–28,41,42], and γ-transition, though not fully understood yet, has been attributed to the relaxation of side chains [28,41,42]. However, γ-transition peak of HDPE 939 appeared at $-125°C$ with an intensity comparable to that of the other LLDPEs. Since HDPE 939, whose density is lower than the usual HDPE probably due to the quenching process during the sample preparation procedure, contains few side chains, γ-transition should be a result of the limited motions such as the crankshaft motion involving $4 \sim 6$ bonds of the main backbone chain.

Fig. 14 compares tan δs of MH 918 and MD 918 with that of ZH 918 having the same density. β-transition of ZH 918 appeared at a temperature similar to that of MH 918 and MD 918. On the contrary, γ-transition was dependent of the type of LLDPEs. γ-transition peak of ZH 918 was weaker in intensity and appeared at a lower temperature compared to that of MH 918 or MD 918. Starck [43] also observed that a metallocene LLDPE showed stronger β-transition and γ-transition peak intensities than a commercial Z–N LLDPE mainly due to the difference in the homogeneity of comonomer composition distribution.

Acknowledgements

References

[1] Bushick RD. J Polym Sci Part A 1965;3:2047.
[2] Burifeld DR, Kachiwa N. Makromol Chem 1985;186:2657.
[3] Kimura K, Shigemura T, Yuasa S. J Appl Polym Sci 1984;29:3161.
[4] Wild L, Ryle TR, Knobeloch DC, Peat IR. J Polym Sci Polym Phys Ed 1982;20:441.
[5] Nakano S, Goto Y. J Appl Polym Sci 1981;26:4217.
[6] Bergtrom C, Avena E. J Appl Polym Sci 1979;23:163.
[7] Crowdbury J, Moore S. Chem Engng News. April 1993;34.
[8] Fink G, Mülhaupt R, Brintzinger HH. Ziegler catalysts, New York: Springer, 1995. p. 35.
[9] Swogger KW, Soga K. Catalyst design for tailor-made polyolefins, Tokyo: Kodansha-Elsevier, 1994. p. 285.
[10] Kaminsky W. Macromol Chem Phys 1996;197:3907.
[11] Macosko CW. Chap. 11. Rheology principles, measurements and application, New York: VHC publishers, 1994.
[12] Stevens JC, Soga K. Catalyst design for tailor-made polyolefins, Tokyo: Kodansha-Elsevier, 1994. p. 277.
[13] Swogger KW, Kao CI. Proceedings of SPE Polyolefins VII International Conference, 1993 February.
[14] Chum PS. Third International Business Forum on Specialty Polyolefins, SPO Conference, September 1993.
[15] Lai S, Knight GW. Dow constrained geometry catalyst technology (CGCT): new rules for ethylene α-olefins interpolymers-controlled rheology polyolefins. SPE Antec'93 Conference Proceedings Technical Papers, XXXIX, 1993. p. 1188.
[16] Bensason S, Minick J, Moet A, Chum S, Hiltmer A, Baer E. J Polym Sci Polym Phys Ed 1996;34:1301.
[17] Brintzinger HH, Fischer D, Mülhaupt R, Rieger B, Waymouth R. Angew Chem Int Ed Engng 1995;107:1255.
[18] Kaminsky W. Catal Today 1994;20:257.
[19] Gupta VK, Satish S, Bhardwag IS. J Macromol Sci, Rev Macromol Chem Phys 1994;C34:439.
[20] Bochmann M. J Chem Soc Dalton Trans 1996;255.
[21] Yoon JS, Lee YS, Park ES, Lee IM, Park DK, Jung SO. To appear in Eur Polym J.
[22] Wilfong D. J Polym Sci Polym Phys Ed 1990;28:861.
[23] Seguela R, Rietsch F. J Mater Sci Lett 1990;9:46.
[24] Yamada K, Takayanagi M. J Appl Polym Sci 1979;24:781.
[25] Plaza AR, Ramos E, Manzur A, Olayo R, Escobar A. J Mater Sci 1997;32:549.
[26] Boyd RH. Polymer 1985;26:1123.
[27] Boyer RF. J Macromol Sci Phys 1973;B8:503.
[28] Khanna YD, Turi EA, Taylor TJ, Vickroy VV, Abbot RF. Macromolecules 1985;18:1302.
[29] Wunderlich B. Macromolecular Physics, 3. New York: Academic press, 1980.
[30] Encyclopedia of polymer science and engineering, 2. New York: Wiley, 1985. p. 478.
[31] Collette JW, Ovenall DW, Buck WH, Ferguson FC. Macromolecules 1989;22:3858.
[32] Petelin A. J Polym Sci 1966;15:427.
[33] Andrews JM, Ward IM. J Mater Sci 1970;5:411.
[34] Capaccio G, Ward IM. Polymer 1974;15:233.
[35] Truss RW, Clarke PL, Duckett RA, Ward IM. J Polym Sci Polym Phys Ed 1984;22:191.
[36] Williamson GR, Wright B, Haward RN. J Appl Chem 1964;14:131.
[37] Warner SB. J Polym Sci Polym Phys Ed 1978;16:2139.
[38] Bastiaansen CWM. J Polym Sci Polym Phys Ed 1990;28:1475.
[39] Deanin RD. Polymer structure, properties and application, New York, PA: The Maple Press, 1972 Chap. 3.
[40] Sehanobish K, Patel RM, Croft BA, Chum SP, Kao CI. J Appl Polym Sci 1994;51:887.
[41] Woo L, Westphal S, Ling TK. Thermochim Acta 1993;226:85.
[42] Sha X, Zhang X, Harrison IR. Thermochim Acta 1991;192:233.
[43] Starck P. Eur Polym J 1997;33:339.