Ethylene–Propylene-α-Olefin Terpolymers Thermal and Mechanical Properties

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ABSTRACT: Thermal and mechanical properties of ethylene–propylene-α-olefin (α-olefin: 1-hexene, 1-decene, and 1-octadecene) terpolymers, obtained with the metallocenic system *rac*-Et[Ind]$_2$ZrCl$_2$/MAO with different comonomer ratios, have been studied. The properties were related to the terpolymer composition and molecular weights. Mechanical behavior of terpolymers was much more influenced by propylene than by α-olefin contents. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3827–3836, 2007

Key words: polyolefins; mechanical properties; thermal properties

INTRODUCTION

One result of the discovery of homogeneous metallocene catalysts is the ability to prepare materials of a defined structure and straight distribution of comonomers and molecular weights. The catalytic system *rac*-Et[Ind]$_2$ZrCl$_2$/MAO has been extensively studied to produce polyethylene, polypropylene, copolymers of ethylene–propylene (EP), and terpolymers of EPDM.[1,2] In the case of the copolymerization of EP, this system is able to incorporate more propene than the unbridged metallocenic systems, nevertheless, the polymers have lower molecular weight than those obtained with the analogous unbridged systems.[3]

Meanwhile, there are a few works on terpolymerizations of ethylene, propylene, and α-olefins. In terpolymerizations with Ziegler–Natta catalysts, a short α-olefin added to the system ethylene-long α-olefin usually facilitates the long α-olefin incorporation in the chain, synergic effect almost unknown with metallocene catalysts.[4,5] Kaminsky and Drogemuller[6] obtained EPO of ethylene/propylene/diene using the metallocenes Cp$_2$ZrCl$_2$ and *rac*-Et[Ind]$_2$ZrCl$_2$/MAO having 6–7 mol % as maximum incorporation of diene. Sepälä and coworkers[4,7] studied the synthesis of co- and terpolymers of ethylene with 1-butene and 1-decene, using Cp$_2$ZrCl$_2$/MAO. They verified that the polymers are completely soluble in *n*-heptane and that there is a significant increase in the catalytic activity assigned to the better monomer diffusion. In the copolymers of ethylene-1-butene and ethylene-1-decene there was a decrease of the molecular weight and increase of activity when compared with the homopolymers. In the terpolymerization of ethylene with 1-butene and 1-octadecene the synergic effect was not observed for the metallocenes bridged or not.

The thermal behavior of ethylene-α-olefin copolymers made with metallocenes has been extensively studied[8–12] and compared with that presented by Ziegler–Natta made copolymers but, to our knowledge, there are no studies on terpolymers.

Mechanical properties of semicrystalline polymers depend on different variables, such as molecular weight, degree of crystallinity, and branching.[13] While the small-strain deformation properties of isotropic polyethylene depend only on crystal content, the large strain tensile deformation properties such as strain at break and tensile toughness depend on the polymer molecular weight in addition to density.[14] The presence of short branches disturbs the crystallization kinetics giving polymers from thermoplastics to elastomers depending on the amount of branching. Many studies are found in the literature about the effect of branching on the crystallization behavior and properties of ethylene/α-olefin copolymers[8,13–16] but there are no studies in terpolymers.[17–19]

In a previous work[20] we showed that the main factor affecting the stress/strain behavior of the ethylene/α-olefin (1-hexene, 1-octene-, 1-decene, 4-methyl-1-pentene, or 1-octadecene) copolymers was the polymer crystallinity. The higher the crystallinity, higher the yield stress and the resistance to strain. Since the degree of crystallinity is directly related to the comonomer content in the polymer (it decreases as the comonomer content increases), it was concluded that there is a strong dependence of the mechanical properties on the comonomer content in copolymers. It was also shown that the type of comonomer scarcely affects the mechanical behavior. Following this work, we synthesized a set of ethylene/propylene/α-olefins (1-hexene, 1-decene, or 1-octadecene) EPO using the metallocene catalyst *rac*-Et[Ind]$_2$ZrCl$_2$/MAO at different comonomer ratios. All the EPO were completely characterized by ^{13}C-NMR[21–23] and in the present work we report the relationship between the terpolymer composition and molecular weights with theirs thermal and mechanical properties.

EXPERIMENTAL

All the polymers were obtained with the *rac*-Et[Ind]$_2$ZrCl$_2$/MAO catalytic system using 2×10^{-5} mol of the catalyst and [Al]/[Zr] ratio of 1500. The co- and terpolymerization reactions were carried out in toluene at α-olefin concentrations of 0.088 and 0.176 mol/L. The polymerization procedure has been described in detail in previous works.[21–23] The ethylene/propylene (E/P) molar ratio (%) in the gas mixture were 95/5, 90/10, 75/25, 50/50, 25/75, 10/90, and 5/95. The ethylene concentration in solution was estimated by using the equation quoted by Kissin[24] and the propylene concentration in toluene during the polymerization reaction was calculated by using the correlation obtained by Villar and Ferreira[1] as described in Ref. 19. Under these conditions in the liquid phase the ethylene and propylene concentration were 0.103 and 0.471 mol/L, respectively, and the E/P concentration ratios [CE/CP (mol/L)] were 0.098/0.016; 0.093/0.032; 0.078/0.079; 0.052/0.158; 0.026/0.237; 0.010/0.285; and 0.005/0.301.

Polymer characterization

The ^{13}C-NMR spectra were recorded at 90°C with an acquisition time of 1.5 s, pulse width of 74° and pulse delay of 4 s on a Varian Inova 300 spectrometer operating at 75 MHz. Under these conditions the spectra are 90% quantitative, considering carbon atoms that have a relaxation time (T_1) shorter than 2.0 s.[25] Sample solution of the polymers were prepared with *o*-diclorobenzene, benzene-d$_6$ (20% v/v) in a 5 mm sample tube. Deuterated solvent was used to provide the internal lock signal.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin–Elmer DSC-4 instrument. The samples were heated from 30 to 160°C and cooled down to 30°C at a heating/cooling rate of 10°C/min. The melting temperature was determined in the second heating. The degree of crystallinity of the co- and terpolymers of ethylene was calculated from ΔH_m equal to 69.4 cal/g[26] for samples obtained with 90 and 95% of ethylene in the gas mixture and from ΔH_m equal to 49.9 cal/g[27] for samples obtained with 90 and 95% of propylene in the gas mixture.

The molecular weight of the polymers was determined by gel permeation chromatography in a Waters GPC 2000 equipped with an optic differential refractometer. A set of three columns, HT6E and HT3 was used. The analyses were performed in 1,2,4-trichlorobenzene at 135°C and 1.0 mL/min. The columns were calibrated with narrow molar mass distribution standards of polystyrene.

Intrinsic viscosity was determined in decahydronaphtalene (decalin) at 135°C by using a Viscosimatic–Sofica viscometer.

Polymers were melt-pressed at 30 to 35°C above their melting point to obtain thin films. Stress/strain experiments were performed at 50 m/min by means of a Universal Test Machine (Wolpert TZZ) at room temperature. At least five specimens of each copolymer were tested. The test specimens had 50-mm gauge length, 10-mm width, and thickness in the range of 0.20–0.30 mm.

RESULTS AND DISCUSSION

Ethylene–propylene copolymers

In this work parent ethylene–propylene copolymers obtained at different E/P ratios and ethylene–propylene-α-olefins terpolymers obtained at two α-olefins concentrations were evaluated, and their thermal and stress–strain behavior were correlated with the chemical composition. The ethylene/propylene mixture was added into the reactor during the whole polymerization and the α-olefins at the very beginning of the reaction. Table I shows the intrinsic viscosities, molecular weights, melting (T_m) and crystallization (T_c) temperatures and crystallinities (X_c) of ethylene–propylene copolymers obtained with different propylene contents.

The commercial high density polyethylene presents DSC melting peak at 135°C. The DSC curves of the ethylene–propylene copolymers having 7.5 (EP5) and 12.2 (EP3) mol % of propylene present intense and well defined melting peaks around 117 and 80°C, respectively. When the propylene content increases, the melting peaks become broader and they shift to lower temperatures, due to the shorter ethylene blocks that crystallize producing smaller or less perfect crystallites if the branches (defects) are

TABLE I
Amount of Incorporated Monomers, Molar Mass and Distribution, Viscosity, and Thermal Properties
of Ethylene—Propylene Copolymers versus Propylene Concentration in the Feed

Sample	Amount of P in the feed (%)	In the copolymer		M_n	M_w	M_w/M_n	Viscosity	T_m	T_c	X_c
		[E] (%)	[P] (%)							
EP 5	5	92.5	7.5	83.100	327.500	3.9	1.8	117.3	102.9	29
EP 3	10	87.8	12.2	65.000	158.600	2.4	1.2	80.4	68.2	13
EP 6	25	64.7	35.3	35.800	80.200	2.2	0.6	a	a	a
EP 7	50	44.3	55.7	—	—	—	—	a	a	a
EP 8	75	29.8	70.2	—	—	—	—	a	a	a
EP 2	90	13.3	86.7	—	—	—	—	96.8	61.1	3
EP 9	95	6.4	93.6	14.500	29.700	2.1	0.3	120.7	92.4	18

$[Zr] = 2 \times 10^{-5}$ mol; Al/Zr = 1500; $T = 40°C$; $P =$ atm; [—], nondetermined; a, amorphous.

excluded from the crystalline phase. However it was pointed out that the incorporation of the methyl branches is also expected to lower the heat of fusion and the melting point, but in this case the lamellae thickness would increase.[15] The samples obtained with 25, 50, and 75% of propylene in the feed (EP6, 7, and 8, respectively) are amorphous at room temperature. In these copolymers the distribution of shorter ethylene sequences is random[21–23] and so the polymer segments are unable to crystallize. Copolymers obtained with higher amount of propylene in the feed, as 90 and 95% or copolymers having 86.7 and 93.6 mol % of propylene, present melting peaks at 97 and 121°C. These copolymers, by its turn, can form isotactic blocks that are able to crystallize. The melting temperature increases with the propylene content, or the longer isotatic blocks, since the isotatic propylene has a melting temperature of 165°C.

The polymers intrinsic viscosity and average molecular weights decrease expressively with the increase of propylene in the feed, due to the increase of termination reactions by the comonomer. The molecular weights distribution or polymer polydispersivity (M_w/M_n) decreases as the propylene content increases, mainly due to the decrease of the molecular weight.

Ethylene–propylene-1-hexene co- and terpolymers

Tables II and III show the intrinsic viscosities, molecular weights, and thermal properties (T_m, T_c, and X_c) of ethylene–propylene-1-hexene terpolymers obtained with 0.088 and 0.176M of 1-hexene in the feed, for different chemical compositions (E, P, and H in mol %). The ethylene-1-hexene copolymer EH 48 (Table II) has a higher melting point than the copolymer EH 49 (Table III), this behavior is expected since the EH 49 copolymer was synthesized with the double amount of 1-hexene, despite the 1-hexene content in both copolymers, determined by ^{13}C-NMR, be almost the same (9.5 and 10 mol %, respectively). On the other hand the higher polydispersity of the EH 49 copoly-

mer (4.1 versus 3.1) seems to have a strong influence in determining the crystallinity and melting temperature. When a low amount of propylene (5% in the gas mixture) is added into the reactor containing 0.088M of 1-hexene, a terpolymer (EPH 38) with lower content of 1-hexene (3.4 mol %) than of propylene (8.0 mol %) is obtained. When the 1-hexene concentration in the feed is 0.176M (two times more) a terpolymer (EPH 39) with inverted composition is obtained, having 8.4 mol % of 1-hexene and 3.9 mol % of propylene. At the lower 1-hexene concentration (0.088M) (Table II), the propylene reduces the 1-hexene incorporation in the growing chain, being preferably incorporated, depressing the terpolymer (EPH 38) T_m to 96.6°C compared with the one (124°C) of the EH 48 copolymer. On the other hand, at higher 1-hexene concentration in the feed (0.176M) (Table III) the propylene does not have the same effect and 1-hexene incorporation in the terpolymer EPH 39 is only slightly reduced, compared with the EH 49 copolymer, being the propylene content lower than in EPH38. In this case the EPH 39 melting temperature (122°C) is higher than the one of the copolymer EH 49 (118°C). The EH49 crystallinity (16%) did not changed whereas it was dramatically reduced when the copolymer has higher propylene content, from 34 (EH48) to 4% (EPH38). So the propylene affects more the terpolymer melting temperature and crystallinity than 1-hexene. Studies on the ethylene-α-olefins copolymers[28,29] concluded that methyl branch is included in the lattice causing a greater influence in the melting temperature and crystallinity than longer branches. However, 3.9 mol % of propylene in the terpolymer EPH 39 it is not enough to reduce the melting temperature and crystallinity to lower values than those of the copolymer EH 49, in which the 1-hexene content is 10 mol % compared with 8.4 mol % in the EPH terpolymer.

Terpolymers of 1-hexene obtained at higher propylene concentration in the feed (10% in the gas mixture), having more than 12 mol % of propene, are amorphous (EPH 40 and 41) independently of the

TABLE II
Amount of Incorporated Monomers, Molecular Weights and Distribution, Viscosity, and Thermal Properties of the Co- and Terpolymers of Ethylene, Propylene, and 1-Hexene Obtained with 0.088 M of 1-Hexene and Different Propylene Amounts in the Feed

| Sample | Propylene in the gas mixture (%) | In the terpolymer | | | M_n (g/mol) | M_w (g/mol) | M_w/M_n | Intrinsic viscosity (dL/g) | T_m (°C) | T_c (°C) | X_c (%) |
		[E]^a (%)	[P]^a (%)	[H]^a (%)							
EH 48	0	90.5	0.0	9.5	121.600	374.400	3.1	1.7	124.3	109.7	34
EPH 38	5	88.6	8.0	3.4	49.800	130.800	2.6	0.9	96.6	77.9	4
EPH 40	10	82.6	14.0	3.4	39.500	91.400	2.3	0.7	a	a	a
EPH 50	25	73.4	24.9	1.7	—	—	—	—	a	a	a
EPH 52	50	53.9	44.4	1.6	—	—	—	—	a	a	a
EPH 54	75	26.0	72.4	1.6	—	—	—	—	a	a	a
EPH 42	90	7.5	91.3	1.3	9.700	19.100	2.0	0.1	88.5	48.3	8
EPH 44	95	3.6	94.0	2.4	9.400	18.200	1.9	0.1	90.6	50.4	8
PH 46	100	0.0	96.9	3.1	12.900	24.200	1.9	0.2	105.0	61.4	19

[Zr] = 2 × 10^{-5} mol, Al/Zr = 1500; T = 40°C; P = atm; [—], nondetermined; a, amorphous.
^{a} Already published in Ref. 22.

TABLE III
Amount of Incorporated Monomers, Molecular Weights and Distribution, Viscosity, and Thermal Properties of the Co- and Terpolymers of Ethylene, Propylene, and 1-Hexene Obtained with 0.176 M of 1-Hexene and Different Propylene Amounts in the Feed

| Sample | Propylene in the gas mixture (%) | In the terpolymer | | | M_n (g/mol) | M_w (g/mol) | M_w/M_n | Intrinsic viscosity (dL/g) | T_m (°C) | T_c (°C) | X_c (%) |
		[E]^a (%)	[P]^a (%)	[H]^a (%)							
EH 49	0	90.0	0.0	10.0	78.400	323.000	4.1	1.8	118.4	101.9	16
EPH 39	5	87.7	3.95	8.4	58.000	219.000	3.8	1.3	122.6	107.3	16
EPH 41	10	81.2	12.7	6.1	41.500	103.000	2.5	0.6	a	a	a
EPH 51	25	70.0	26.2	3.8	—	—	—	—	a	a	a
EPH 53	50	46.1	50.8	3.1	—	—	—	—	a	a	a
EPH 55	75	21.8	77.1	1.1	—	—	—	—	a	a	a
EPH 43	90	5.7	91.8	2.5	9.800	19.200	2.0	0.2	80.5	a	5
EPH 45	95	1.8	93.7	4.5	11.400	22.100	1.9	0.3	87.6	a	10
PH 47	100	0.0	93.5	6.5	12.200	22.900	1.9	0.2	105.9	59.0	16

[Zr] = 2 × 10^{-5} mol, Al/Zr = 1500; T = 40°C; P = atm; [—], nondetermined; a, amorphous.
^{a} Already published in Ref. 22.

1-hexene content, although the copolymer (EP3-Table I) with the same PO content presents melting point at 80.4°C and 13% of crystallinity. In this case 1-hexene determines the terpolymer thermal properties.

Copolymers of ethylene–propylene EP 6–8 and EPO of these obtained at PO concentration in the feed from 25 to 75%, having 24–77 mol % of PO, are amorphous having 1-hexene content lower than 3.8 mol %. Copolymers EP 2 and 9 and EPO of 1-hexene (EPH 42–45) obtained at PO concentration in the feed of 90 and 95%, having 91–94 mol % of PO, and 1-hexene content from 1.3 to 4.5 mol % present T_m and crystallinity. The 1-hexene concentration did not affect the PO incorporation and the ethylene and 1-hexene content changed comparatively. These polymers present shorter polydispersivity and have relatively lower molecular weight since the main monomer in the medium is PO for which the catalyst is not appropriate because of the fast β-elimination reaction. The endothermic curves of the EPO EPH 42–45 showed a significant enlargement and decrease in intensity and melting peaks when compared with the corresponding copolymers (EP 2 and EP 9). However samples EPH 42 and 43 present higher degree of crystallinity compared with the corresponding EP 2 copolymer ($X_c = 3\%$), whereas the crystallinity of the EPH 44 and 45 EPO decreased about 50% related to the value (18%) of the EP 9 copolymer. Higher amounts of PO in the these EPO lead to higher melting points and crystallinities, but even having isotactic PO blocks the T_m values are lower than those of the EPO rich in ethylene.

The propylene-1-hexene copolymers (PH 46 and PH 47) at both 1-hexene concentrations show almost the same melting points, crystallinities and molecular weights, even thought, having different 1-hexene content. It seems that the increase of the amount of 1-hexene in the copolymer from 3.1 to 6.5 mol % it is not enough to affect these parameters. However these copolymers show a significant decrease of melting temperature and crystallinity compared with the homopolymers of PO obtained by metallocenes that are around 135°C and 40%.

PO seems to favors the α-elimination reactions more than 1-hexene, as the polymer molecular weights are reduced when its concentrations in the feed and in the terpolymer increase. Polydispersivities in all cases decrease with the increase in the amount of PO or the decrease in the molecular weights.

Ethylene–propylene-1-decene co- and terpolymers

Tables IV and V show the intrinsic viscosities, molecular weights and thermal properties (T_m, T_c, and X_c) of ethylene–propylene-1-decene EPO also obtained with 0.088 and 0.176M of 1-decene in the feed.

TABLE IV
Amount of Incorporated Monomers, Molecular Weights and Distribution, Viscosity, and Thermal Properties of the Co- and Terpolymers of Ethylene—Propylene and 1-Decene Obtained with 0.088 M of 1-Decene and Different Propylene Amounts in the Feed

| Sample | Propylene in the gas mixture (%) | In the terpolymer | | | M_n (g/mol) | M_w (g/mol) | M_w/M_n | Intrinsic viscosity (dL/g) | T_m (°C) | T_c (°C) | X_c (%) |
		$[E]^a$ (%)	$[P]^a$ (%)	$[D]^a$ (%)							
ED 26	0	92.9	0.0	7.1	94.500	375.000	4.0	2.2	125.0	111.7	39
EPD 16	5	92.0	2.5	5.5	96.000	227.000	2.4	1.3	98.5	78.9	11
EPD 15	10	90.1	6.1	3.8	87.500	197.300	4.2	1.2	71.9	61.9	8
EPD 18	25	67.7	28.9	3.4	—	—	—	—	a	a	a
EPD 20	50	47.2	51.7	1.1	—	—	—	—	a	a	a
EPD 23	75	27.4	72.2	0.5	—	—	—	—	a	a	a
EPD 27	90	12.8	85.9	1.3	—	—	—	—	76.5	52.7	1
EPD 25	95	9.1	89.7	1.2	—	—	—	—	86.5	65.3	3
PD 32	100	0.0	95.6	4.4	9.700	19.700	2.0	0.1	113.7	67.6	11

[Zr] = 2 × 10⁻⁵ mol; Al/Zr = 1500; T = 40°C; P = atm; [—], nondetermined; a, amorphous.
a Already published in Ref. 21.

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TABLE V
Amount of Incorporated Monomers, Molecular Weights and Distribution, Viscosity, and Thermal Properties of the Co- and Terpolymers of Ethylene, Propylene and 1-Decene Obtained with 0.176 M of 1-Decene and Different Propylene Amounts in the Feed

Sample	Propylene in the gas mixture (%)	In the terpolymer			M_n (g/mol)	M_w (g/mol)	M_w/M_n	Intrinsic viscosity (dL/g)	T_m (°C)	T_c (°C)	X_c (%)
		$[E]^a$ (%)	$[P]^a$ (%)	$[D]^a$ (%)							
ED 30	0	85.6	0.0	14.4	80.000	325.400	4.1	1.7	125.6	113.0	32
EPD 14	5	89.3	2.3	8.4	93.300	232.800	2.5	1.3	80.9	53.7	3
EPD 13	10	86.8	6.3	6.9	81.600	189.600	2.3	1.2	70.0	46.9	2
EPD 17	25	67.1	27.6	5.4	—	—	—	—	a	a	a
EPD 19	50	40.5	52.5	7.0	—	—	—	—	a	a	a
EPD 21	75	31.3	66.1	2.6					a	a	a
EPD 28	90	14.5	84.8	0.8	13.200	26.800	2.0	0.2	a	a	a
EPD 24	95	4.4	93.3	2.3	10.600	21.900	2.1	0.2	a	a	a
PD 33	100	0.0	95.1	4.9	9.500	18.300	1.9	0.1	108.4	70.9	15

[Zr] = 2 × 10⁻⁵ mol; Al/Zr = 1500; T = 40°C; P = atm; [—], nondetermined; a, amorphous.
ᵃ Already published in Ref. 21.

The copolymers ED 30 and 26 present almost the same melting point and crystallinity, even having the former higher 1-decene (14.4 mol %) content than the last (7.1 mol %). These results are unpredictable and may be attributed to a different 1-decene distribution in the chain but with lamellas or crystallites been quite similar. The polydispersivities of the ED copolymers are similar to EH ones and around 4.0. Terpolymer EPD 14 has more 1-decene content than the EPD 16 and same PO content, presenting lower melting point and crystallinity. The EPO EPD 15 and 13 obtained with 10% of PO in the feed, contrary to the 1-hexene ones, present T_m and some crystallinity although the endothermic curve profiles are badly defined and the values are not very precise. Both melting points and crystallinities of these EPD EPO are lower than the corresponding copolymer EP 3. The number average molecular weights of the 1-decene EPO with low amount of propene did not change so much and are quite similar to the ones of the ED copolymers suggesting a lower chain transfer to PO or 1-decene compared with the ethylene–propylene copolymers and EPO of 1-hexene. This can be explained by the higher amount of incorporation of PO in the copolymer (EP3 = 12.2 mol %) and EPO of 1-hexene (EPH40 = 14.0 and 41 = 12.7mol%) compared with the EPO with 1-decene (EPD 15 = 6.1 mol % and EPD 13 = 6.3 mol %) for the same amount of propene in the feed.

As seen for the 1-hexene EPO, amounts of PO in the feed from 25 to 75% lead to amorphous EPO at room temperature. For PO amounts higher than 90% in the feed, only the EPO (EPD 27 and 25), obtained at 0.088M of 1-decene, present very low crystallinity and so melting point. As commented before increasing the PO content in the polymer leads to isotactic poly PO blocks that can crystallize giving melting points similar to the EPO rich in ethylene. At 0.176M of 1-decene, the EPO (EPD 24 and 28) did not show crystallinity and so neither melting point. The copolymer PD 33 (D = 4.9 mol %) shows a lower melting temperature than PD 32 (D = 4.4 mol %) corresponding to the difference in 1-decene content, however the crystallinity is higher, but the difference is not significant.

Ethylene–propylene-1-octadecene co- and terpolymers

Tables VI and VII show the intrinsic viscosities, molecular weights and thermal properties (T_m, T_c, and X_c) of ethylene–propylene-1-octadecene EPO obtained at the same conditions of those with 1-hexene and 1-decene. Compared with 1-hexene and 1-decene, the 1-octadecene reduces more efficiently the crystallinity or even prevents it totally in copolymers

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TABLE VI
Amount of Incorporated Monomers, Molecular Weights and Distribution, Viscosity, and Thermal Properties of the Co- and Terpolymers of Ethylene, Propylene, and 1-Octadecene Obtained with 0.088 M of 1-Octadecene and Different Propylene Amounts in the Feed

Sample	Propylene in the gas mixture (%)	In the terpolymer			M_n (g/mol)	M_w (g/mol)	M_w/M_n	Intrinsic viscosity (dL/g)	T_m (°C)	T_c (°C)	X_c (%)
		[E]ᵃ (%)	[P]ᵃ (%)	[O]ᵃ (%)							
EO 56	0	90.9	0.0	9.1	150.900	415.200	2.8	1.6	121.3	105.8	21
EPO 58	5	91.4	4.2	4.4	75.500	166.100	2.2	1.3	95.2	77.0	6
EPO 60	10	88.3	9.7	2.1	48.950	104.700	2.1	1.3	a	a	a
EPO 62	25	65.8	29.1	5.1	39.400	78.500	2	1.3	a	a	a
EPO 64	50	65.2	32.1	2.7	—	—	—	—	a	a	a
EPO 66	75	45.1	50.8	4.1	15.300	30.500	2	—	a	a	a
EPO 68	90	15.2	83.7	1.1	11.300	21.800	1.9	0.1	a	a	a
EPO 70	95	9.4	86.8	3.8	18.900	35.050	1.9	—	a	a	a
PO 72	100	0.0	95.8	4.2	15.900	31.150	2	—	109.3	56.7	8

[Zr] = 2 × 10⁻⁵ mol; Al/Zr = 1500; T = 40°C; P = atm; [—], nondetermined; a, amorphous.
ᵃ Already published in Ref. 23.

TABLE VII
Amount of Incorporated Monomers, Molecular Weights and Distribution, Viscosity, and Thermal Properties of the Co- and Terpolymers of Ethylene, Propylene, and 1-Octadecene Obtained with 0.176 M of 1-Octadecene and Different Propylene Amounts in the Feed

Sample	Propylene in the gas mixture (%)	In the terpolymer			M_n (g/mol)	M_w (g/mol)	M_w/M_n	Intrinsic viscosity (dL/g)	T_m (°C)	T_c (°C)	X_c (%)
		[E]ᵃ (%)	[P]ᵃ (%)	[O]ᵃ (%)							
EO 57	0	89.8	0.0	10.2	—	—	—	1.2	104.0	98.4	7
EPO 59	5	88.5	3.3	8.2	66.400	148.400	2.2	1.1	94.6	75.6	3
EPO 61	10	81.0	10.3	8.7	46.300	94.900	2.1	0.6	a	a	a
EPO 63	25	59.9	31.9	8.2	45.600	85.600	1.9	0.5	a	a	a
EPO 65	50	56.6	39.7	3.7	—	—	—	—	a	a	a
EPO 67	75	—	—	—	19.500	37.200	1.9	—	a	a	a
EPO 69	90	12.0	82.4	5.6	—	—	—	—	a	a	a
EPO 71	95	8.9	84.8	6.4	18.750	34.200	1.8	—	a	a	a
PO 73	100	0.0	87.0	13.0	21.600	38.300	1.8	—	a	a	a

[Zr] = 2 × 10⁻⁵ mol; Al/Zr = 1500; T = 40°C; P = atm; [—], nondetermined; a, amorphous.
ᵃ Already published in Ref. 23.

with propylene (PO) and terpolymers (EPO). Only the EPO having 5% of PO in the feed present some crystallinity around 6 and 3%, the other 1-octadecene EPO are totally amorphous at room temperature as well as the propylene-1-octadecene copolymer (PO 73). This confirm that longer branches inhibit the crystallization process much more effectively than shorter branches as it was already notice in copolymers.[16] The more 1-octadecene incorporates in the polymer lower are the crystallinity and melting point. As expected PO depresses significant the crystallinity and melting point of ethylene–propylene-α-olefin EPO compared with the ethylene- or propylene-α-olefin copolymers. However the differences in melting point between the two EPO obtained with the same amount of PO (5% in the feed) and different amount of 1-octadecene is not significant. In fact, terpolymer EPO 58 has higher incorporation of PO (4.2 mol %) than EPO 59 (3.3 mol %) but lower amount of 1-octadecene (4.4 mol %) compared with EPO 59 (8.2 mol %). All the other EPO of 1-octadecene are amorphous not presenting melting temperatures or crystallinities at room temperature, even those with more than 80 mol % of PO.

Mechanical properties

Only the copolymers of ethylene-α-olefins and the EPO obtained with E/P gas mixture (%) of 95/5 and 90/10 had their mechanical properties evaluated. The other EPO were too sticky for film preparation.

Figure 1 shows the stress–strain behavior of ethylene-1-hexene copolymers and ethylene–propene-1-hexene EPO. The copolymers show very different stress–strain curves for little differences in comonomer content but differences in crystallinity. In fact,
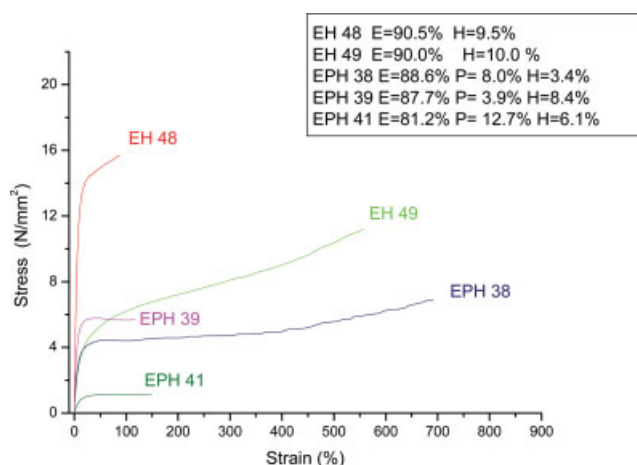

Figure 2 Stress–strain curves of ethylene-1-decene copolymers and ethylene–propene-1-decene terpolymers with different comonomer contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].
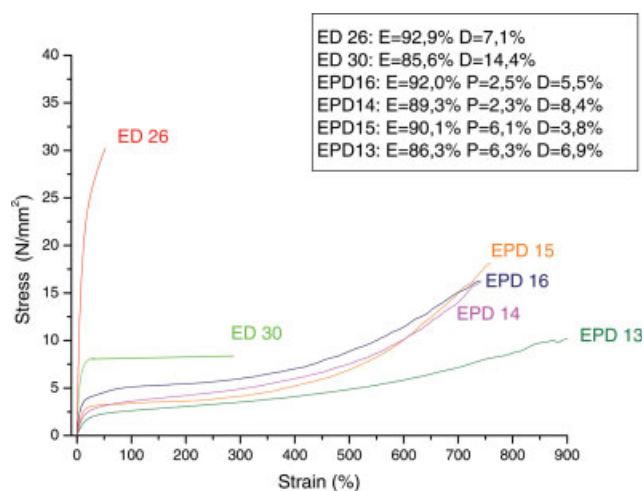
the EH 48 presents 9.5 mol % of 1-hexene and 34% of crystallinity and the EH 49 10.0 mol % and 16%, respectively. The EH 48 presents high modulus, low deformation and plastic behavior. On the other hand, sample EH49 shows elastomeric behavior with a low modulus and high strain, being a strength material. In the EPO the modulus seems to be affected more by the PO content and less by the 1-hexene content. In fact, sample EPH39 with the highest 1-hexene content (8.4 mol %) presents the highest crystallinity and modulus among the EPO because of the lowest PO content (3.9 mol %). Sample EPH38 has a PO content of 8.0 mol % and the lowest 1-hexene content (3.4 mol %) having 4% of crystallinity, its behavior is intermediate between that of samples EPH41 (amorphous, with the lowest modulus and molecular weight averages and the highest PO content, 12.7 mol %) and EPH 39 with the lowest PO content and higher crystallinity.

Figure 2 shows the stress–strain curves of ethylene-1-decene copolymers and ethylene–propene-1-decene EPO. The copolymers stress–strain profiles are quite different because of their differences in crystallinity and in 1-decene content, in fact sample ED26 has a crystallinity of 39% and a 1-decene content of 7.1 mol % and sample ED 30, 32% and 14.4 mol %. The EPO stress–strain curves seem to be more influenced by the PO than by 1-decene content. EPD16 and EPD14 present almost the same PO content (2.5 and 2.3 mol %, respectively) and the curves are much closed, nevertheless EPD 16 has higher crystallinity (11% compared with 3%). Due to the inferior 1-decene content (5.5 versus 8.4 mol %), this influence much more the modulus than the material resistance. Samples EPD15 and EPD13 present similar PO contents (6.1 and 6.3, respectively) having the
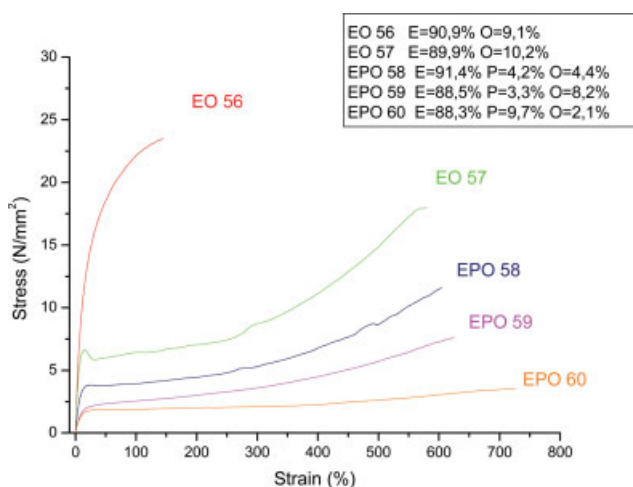

Figure 1 Stress–strain curves of ethylene-1-hexene copolymers and ethylene–propene-1-hexene terpolymers with different comonomer contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

Figure 3 Stress–strain curves of ethylene-1-octadecene copolymers and ethylene–propene-1-octadecene terpolymers with different comonomer contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

last one higher 1-decene content (6.9 versus 3.8 mol %) and lower crystallinity and thus showing lower modulus. The big difference in 1-decene content between samples EPD14 and EPD15 (8.4 and 3.8 mol %) did not significantly modified the stress–strain profile.

The stress–strain curves of ethylene-1-octadecene copolymers and ethylene–propene-1-octadecene EPO are shown in Figure 3. EO56 and EO57 copolymers curves profile is quite different because of their crystallinity (21 and 7%, respectively) in spite of the low differences in 1-octadecene content (9.1 and 10.2 mol %, respectively). The EO56 is a more rigid material with strain at break around 150, whereas the EO 57 presents yield point and a strain at break around 550%. EPO behavior shows also to be more influenced by the PO content than by the 1-octadecene content, even though this last one has also some influence. The PO incorporation decreases more effectively the polymer crystallinity. On the other hand, samples EPO58 and EPO59 with close PO contents (4.2 and 3.3 mol %, respectively) but quite different in 1-octadecene content (4.4 and 8.2 mol %, respectively) show the influence of 1-octadecene that depresses even more the crystallinity and also lows the modulus. Sample EPO60 with the highest PO content (9.7 mol %) and the lowest 1-octadecene content (2.1 mol %) is an amorphous material and presents the lowest modulus and the higher strain, confirming the higher influence of PO in the mechanical properties. Comparing samples EPH 39 ($P = 3.9$ mol %, $H = 8.4$ mol %), EPD 14 ($P = 2.3$ mol %, $D = 8.4$ mol %) and EPO 59 ($P = 3.3$ mol %, $O = 8.2$ mol %) with close values of comonomers and viscosities (1.3, 1.3, and 1.1 dL/g, respectively), EPO with smaller side chain (1-hexene) has the highest

modulus and the lowest strain compared with the EPO with 1-decene and 1-octadecene that have lower modulus but quite higher strains. This shows that longer branches, higher than C_4, depress much more the mechanical properties than the shorter ones as discussed in a previous works with copolymers.[30]

CONCLUSIONS

Increasing the PO content in ethylene–propylene-α-olefins EPO decrease the chain ethylene crystallizable segments depressing the polymer melting temperature and crystallinity. When the terpolymer contains a significant amount of ethylene and PO the polymer is amorphous. There is a random distribution[21–23] of both monomers producing short segments of ethylene or PO, enables to crystallize. When the amount of PO increases, the isotactic blocks of PO crystallize, increasing the melting temperature. The molecular weight decreases with the increase of PO incorporated in the polymer chain in a higher degree that when the amount of α-olefin increases.

Ethylene-α-olefin copolymers mechanical properties showed to be highly influenced by comonomer content. The EPO of ethylene–propylene/α-olefin present lower modulus than ethylene/α-olefin copolymers and all present elastomeric behaviors. Mechanical behavior of EPO was much more influenced by PO than by α-olefin contents. On the other hand, 1-decene and 1-octadecene branches depressed much more the mechanical properties than 1-hexene. Long branches as hexyl, octyl, or hexadecyl normally are not able to enter the crystalline phase, forming a thin interphase inside the amorphous domain. It is generally accepted that methyl branches from PO are included in the crystalline lattice.[28,29] This fact explains the dramatic modification of the EPO modulus with the increase of PO content.

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