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Study of Ethylene-Propylene-1-Hexene Co- and Terpolymers Obtained with Homogeneous and Supported Metallocene Catalysts

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Summary: Ethylene-propylene-1-hexene terpolymers were obtained using three metallocenic systems: Cp_2ZrCl_2, Cp_2ZrCl_2 directly supported on silica (Cp_2ZrCl_2/SiO_2) and Cp_2ZrCl_2 supported on MAO (methylaluminoxane)-modified silica ($Cp_2ZrCl_2/MAO/SiO_2$). The results were compared with those obtained with *rac*-Et[Ind]$_2$ZrCl$_2$. The best activities were obtained with the Cp_2ZrCl_2 in the homogeneous form, but the system $Cp_2ZrCl_2/MAO/SiO_2$ afforded also good results. Those systems showed to be able to incorporate enough comonomers, in a randomic way, to give terpolymers with an elastomeric behaviour.

Keywords: mechanical properties; metallocene catalysts; NMR; polyolefins; structure-property relations

Introduction

The metallocenes are single site catalysts. Therefore, they allow a high control of the microstructure of the polymers, such as, narrow molar weight distribution ($Mw/Mn \approx 2$), narrow comonomer distribution in copolymerization and they also copolymerize bulk monomers which do not react with the traditional Ziegler-Natta catalysts.[1] The α-olefins produce, in general, a positive effect on the catalytic activity in the copolymerization with ethylene (comonomer effect).[2] In fact, metallocenes are excellent for copolymerization compared with other catalytic systems. To obtain an ethylene-1-butene copolymer with 0.92 g/cc density it is necessary a molar ratio of $C_4/C_2 = 0.35$ with a Ziegler-Natta catalyst, $C_4/C_2 = 0.083$ with a chromium oxide catalyst and $C_4/C_2 = 0.02–0.03$ with a metallocene catalyst.[3] The copolymerization depends on the catalyst structure: Metallocenes with bridge incorporate more comonomer and produce polymers with higher molecular weight than those without bridge. However, non-bridged metallocenes supported on silica presented much higher catalytic activities than bridged ones.[4] The use of inert supports for metallocene heterogeneisation is employed to adapt such catalysts to industry (slurry or gas-phase processes), to decrease the amount of MAO, to control polymer morphology and to prevent reactor fouling.[5]

In previous a work[6] we obtained ethylene-propylene-1-hexene terpolymers with the homogeneous metallocene *rac*- EtInd$_2$-ZrCl$_2$ and determined the chemical shifts, triads and reactivity ratios by ^{13}C NMR. In the present work we aim to study the use of supported metallocenic systems to obtain terpolymers, to compare the results with those obtained with homogeneous metallocenes and to correlate the molecular structure of the terpolymers with the mechanical properties. The metallocene Cp_2ZrCl_2 was chosen to support because is the simplest and cheapest one among the non-bridged

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metallocenes and it can be a good option to be used industrially.

Catalytic Systems

Two supported catalytic systems were prepared and compared with the homogeneous Cp_2ZrCl_2. The first supported system was the Cp_2ZrCl_2 supported directly on Silica Grace 956 previously activated at 450 °C during 16 h at 10^{-4} mbar. 1.0 wt% of metallocene was supported by the grafting method during 1 h at room temperature. The supported metallocene was washed 10 times with 2 ml of toluene. The second method used Silica Grace 956 impregnated with 2.0 wt % of methylaluminoxane (MAO), prior to the catalyst grafting. The effective amount of zirconium catalyst supported was 0.44 wt% Zr/SiO_2 for Cp_2ZrCl_2/SiO_2 and 0.55 wt% Zr/SiO_2 for $Cp_2ZrCl_2/MAO/SiO_2$, calculated using Rutherford Backscattering Spectrometry (RBS).[7] The two supported catalysts will be named as Cp_2ZrCl_2/SiO_2 (CpSi) and $Cp_2ZrCl_2/MAO/SiO_2$ (CpMAOSi) respectively. The catalysts were tested in the terpolymerization of ethylene, propylene and 1-hexene. Four different ethylene/propylene ratios (E/P = 95/5, 90/10, 80/20 and 75/25) and a constant concentration of 1-hexene (0.176 M) were employed. Ratios of E/P lower than 75/25 were not used because the activity decreased, significantly, with the increase of the amount of propylene. Figure 1 shows the behavior of the catalytic activity with the three catalytic systems with increasing amount of propylene in the feed. The activities of supported systems were compared with those obtained with homogeneous metallocenes Cp_2ZrCl_2 and *rac*-$EtInd_2ZrCl_2$.[8]

The catalytic activities obtained with Cp_2ZrCl_2 were superior to those obtained with *rac*-$EtIndZrCl_2$ in all cases, even with the supported systems. Among the supported catalysts, the system with MAO, showed the best results. In all cases, a positive comonomer effect of propylene was verified for low propylene/ethylene ratios. This effect was more pronounced for the most actives catalytic systems: Homogeneous Cp_2ZrCl_2 (upon P/E = 0.11) and Cp_2ZrCl_2/ MAO/SiO_2 (upon P/E = 0.25).

Table 1 shows the comonomer amounts incorporated in the terpolymers, molecular weights, melting points and crystallinities as a function of the E/P ratio in the feed.

The catalytic system Cp_2ZrCl_2/SiO_2 incorporates less comonomer than the homogeneous Cp_2ZrCl_2 and the supported $Cp_2ZrCl_2/MAO/SiO_2$. The molecular weights of the terpolymers obtained with the supported systems are higher than those

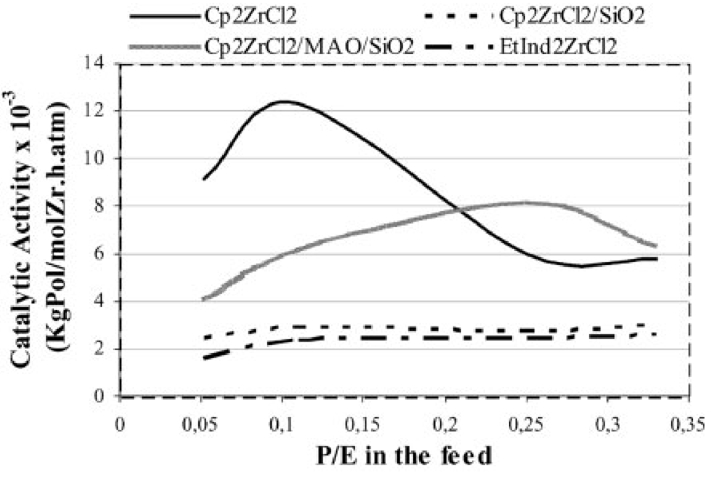

Figure 1.

Catalytic activities obtained with the catalytic systems Cp_2ZrCl_2, Cp_2ZrCl_2/SiO_2, $Cp_2ZrCl_2/MAO/SiO_2$ and *rac*-$EtIndZrCl_2$.

Table 1.
Comonomer incorporation, molecular weighs and thermal properties.

E/P	[H] (mol%)	[P] (mol%)	Mw (g/mol)	Mw/Mn	Tm (°C)	χc (%)
Cp_2ZrCl_2						
95/5	2.2	0.2	14100	1.7	110.2	32
90/10	0.7	2.9	9500	2.9	113.8	47
80/20	2.8	3.5	9800	1.8	99.8	30
75/25	3.1	3.2	12500	1.5	96.9	22
Cp_2ZrCl_2/SiO_2						
95/5	1.3	0.4	41400	2.7	113.0	33
90/10	1.3	1.1	37600	1.7	112.8	35
80/20	1.8	2.6	14000	1.8	105.1	29
75/25	2.1	3.0	25800	1.9	100.3/124.8	14/6
$Cp_2ZrCl_2/MAO/SiO_2$						
95/5	1.8	0.5	153200	2.1	112.8	37
90/10	2.3	1.5	74250	2.0	107.6	30
80/20	1.5	3.8	111250	1.8	99.8	30
75/25	3.0	5.5	57000	1.8	94.8	16

obtained with the homogeneous system as is usual for supported catalysts.[4,5] The supported system impregnated with MAO showed higher molecular weight than that directly supported on silica. The molecular weight distribution was close to 2 in all cases, showing that the single site nature of the metallocene was kept on the supported catalyst. Melting temperatures and crystallinities are in accord with the respective incorporations of comonomers. It is worth noticing that the amount of incorporated propylene grows with the increase of propylene in the feed, but the amount of 1-hexene, even though it was maintain constant in the reactional medium, varies. This fact suggests a competition of this comonomer with propylene for the active site during the polymerization reaction.

Table 2 shows the triad sequence distribution of the terpolymers obtained by ^{13}C NMR. All the terpolymers are random. Generally, methyl and butyl branches are isolated between ethylene blocks.

Comparing the homogeneous metallocene with bridge (*rac*-EtInd$ZrCl_2$) with the non-bridged one, the latter incorporates much less comonomer, as shown in Figure 2.

To correlate with the molecular structure of the terpolymers, the mechanical

Table 2.
Triad sequence distribution of the EPH terpolymers in mol%.

E/P	[EEE]	[EEP + PEE]	[PEP]	[EEH + HEE]	[HEH]	[EPE]	[EHE]	[EHH + HHE]
Cp_2ZrCl_2								
95/5	93.3	0.5	0	4.0	0	0.2	2.1	0
90/10	88.9	5.7	0.3	1.4	0.06	2.9	0.7	0
80/20	84.8	5.0	0	3.9	0	3.5	2.8	0
75/25	85.1	7.2	0	4.4	0	3.3	1.4	0
Cp_2ZrCl_2/SiO_2								
95/5	95.3	0.5	0	2.5	0	0.4	1.3	0
90/10	92.7	2.3	0	2.6	0	1.1	1.3	0
80/20	92.6	3.0	0	0.0	0	2.6	1.8	0
75/25	88.3	6.1	0	0.5	0	3.0	2.1	0
$Cp_2ZrCl_2/MAO/SiO_2$								
95/5	94.1	0.8	0	2.9	0	0.5	1.8	0
90/10	90.7	2.1	0	3.4	0	1.5	2.3	0
80/20	82.7	7.0	0.5	3.7	0	3.7	2.3	0
75/25	76.9	9.4	0.5	4.6	0	5.0	2.6	0.4

[EPP+PPE] = [PPP] = [HPP+PPH] = [HPH = [PHP] = [HHP+PHH] = 0.

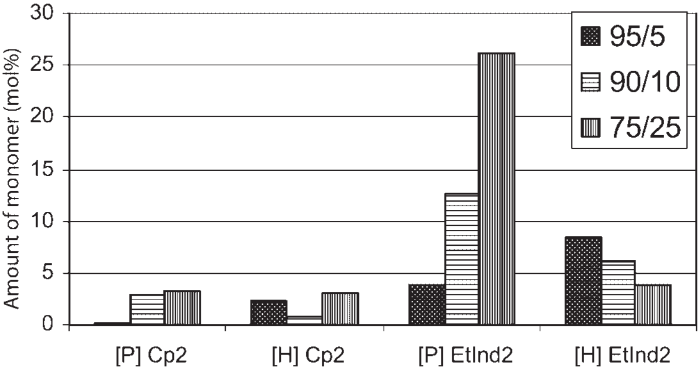

Figure 2.
Comparative of propylene and 1-hexene incorporation between Cp_2ZrCl_2 and *rac*-EtIndZrCl$_2$ in EPH terpolymerization.

properties were studied by dynamic mechanical analysis The storage modulus and the tan delta of the EPH terpolymers obtained with Cp_2ZrCl_2 are shown in Figures 3 and 4.

Dynamic storage modulus (E′) is approximately similar to the Young or elastic modulus or stiffness.[9] The elastic modulus is related to crystallinity, and normally increases with crystallinity at a given temperature. In the case of EPH terpolymers, the storage modulus decreases with the increase of 1-hexene in the terpolymer which is also related with the decrease of crystallinity and does not follow any defined trend with the amount of propylene. In fact, Fig. 3 shows that the terpolymer with lower amount of 1-hexene (0.7mol%) and amount of propene 2.9mol% presents higher crystallinity (Xc = 47%) and higher modulus than the terpolymer with higher amount of 1-hexene (2.2mol%) and lower amount of propylene (0.2mol%) and Xc = 32%. This shows that 1-hexene content influences more that the propylene amount

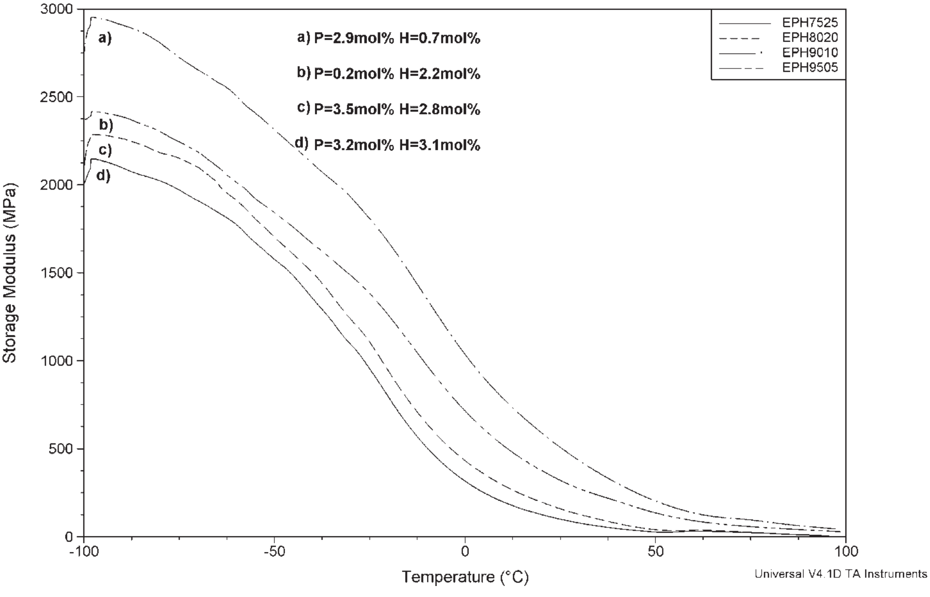

Figure 3.
Storage Modulus of the EPH terpolymers obtained with Cp_2ZrCl_2.

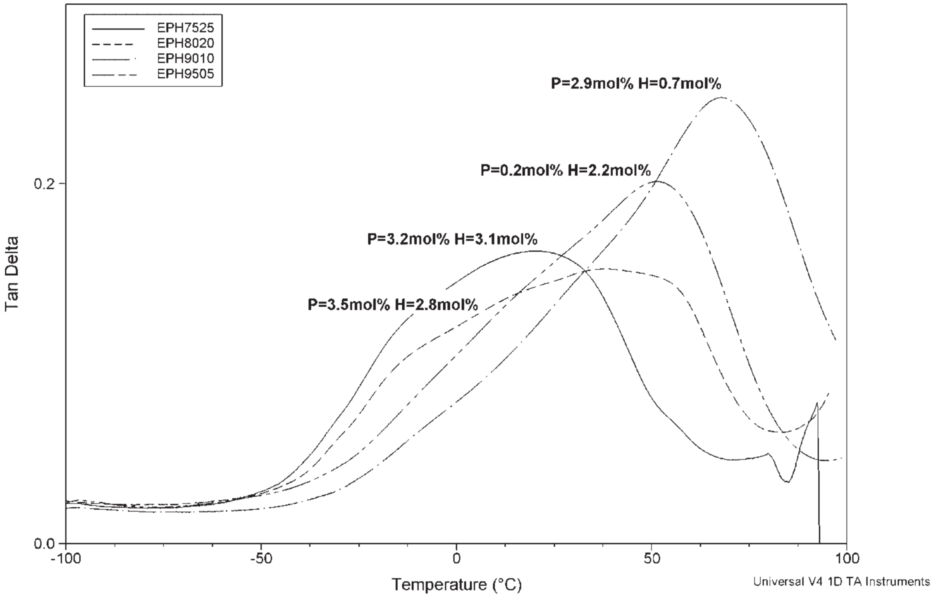

Figure 4.
Tan Delta of the EPH terpolymers obtained with Cp_2ZrCl_2.

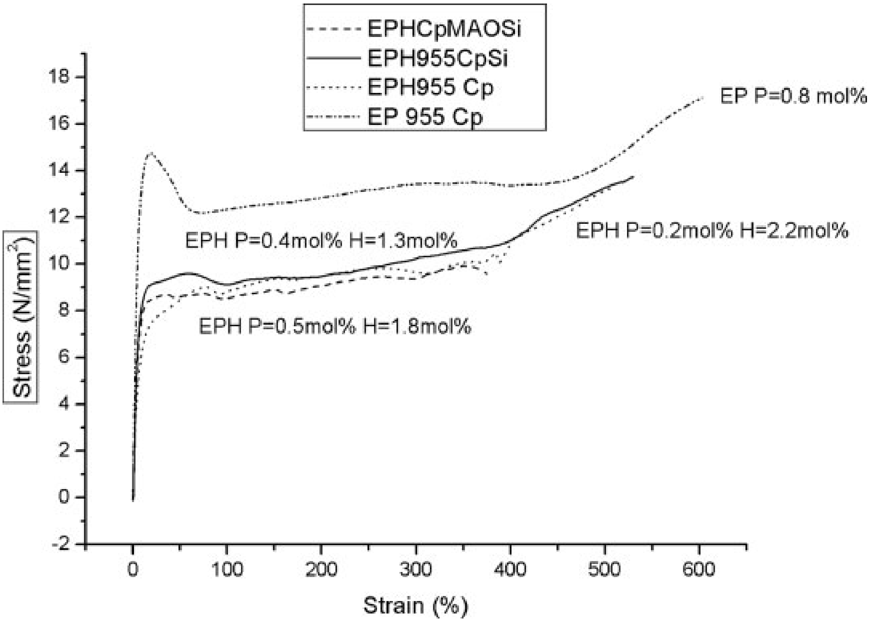

Figure 5.
Mechanical properties of a EP copolymer and EPH terpolymers obtained with different catalytic systems using E/P ratio of 95/5 and [H] = 0.176 M in the feed.

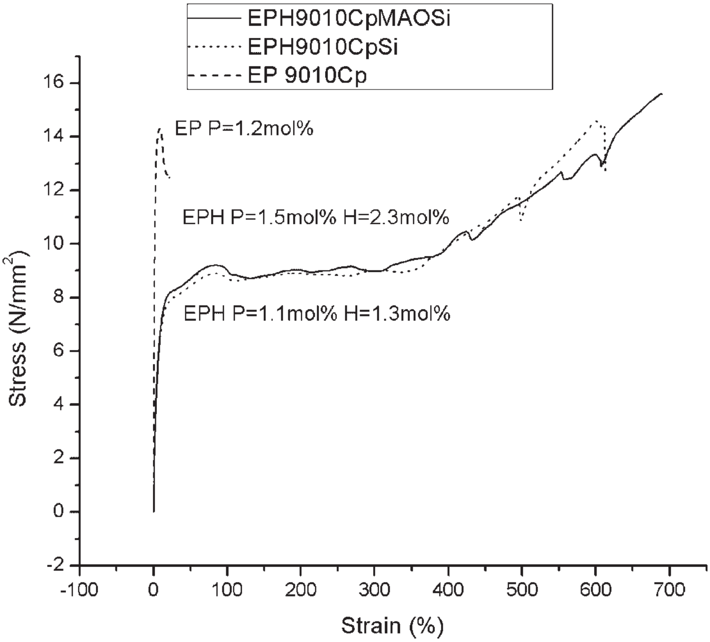

Figure 6.

Mechanical properties of an EP copolymer and EPH terpolymers obtained with different catalytic systems using E/P ratio of 90/10 and [H] = 0.176 M in the feed.

in these properties. This behavior can also be observed in the Tan δ.

Tan δ shows the α transition. Tα is determined by the average thickness of the lamellae and its intensity grows with increasing crystallinity. This transition is not observe without amorphous phase and it is attributed to the deformation of amorphous

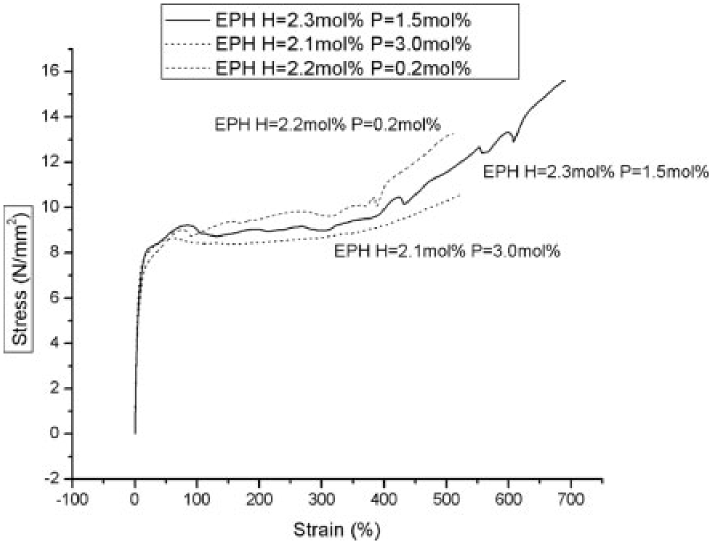

Figure 7.

Mechanical properties of EPH terpolymer obtained with different catalytic systems and with a similar incorporation of 1-hexene (≈2 mol%).

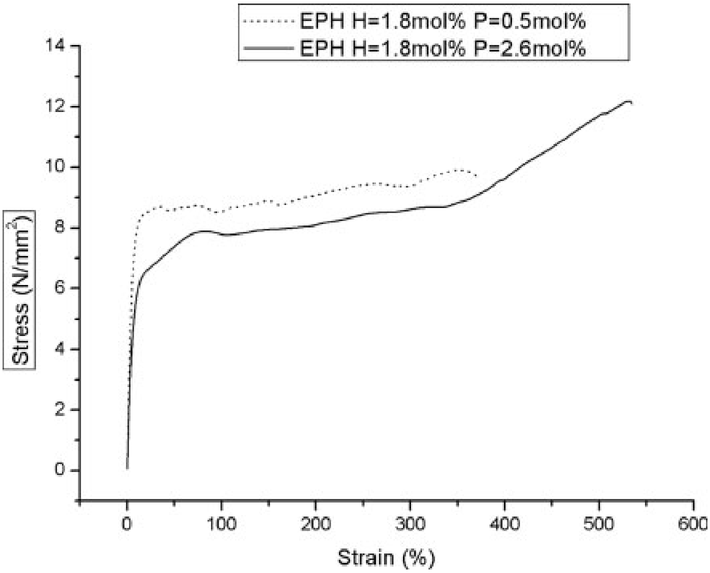

Figure 8.
Mechanical properties of EPH terpolymer obtained with different catalytic systems and with a similar incorporation of 1-hexene (≈1.8 mol%).

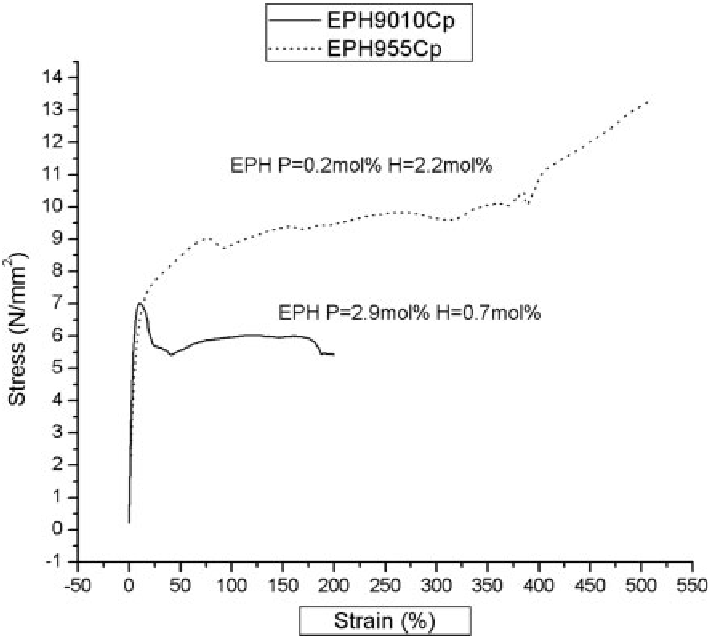

Figure 9.
Mechanical properties of the EPH terpolymers obtained with same catalyst systems: Cp_2ZrCl_2 using the different E/P ratios and $[H] = 0.176$ M in the feed.

regions due to the reorientation of the crystallites and also to the deformation of chain segments within the folds and loops of the interfacial region.[10]

As it is stated in other works,[11] the methyl branch of propene is part of the crystal lattice and it can influence the crystallinity but not the amorphous phase. On the other hand, butyl branch from 1- hexene is excluded from the crystal lattice and its amount has a strong influence on the amorphous phase, affecting the dynamic mechanical properties. Figure 4 also shows a shoulder close to −10 °C for the two more branched samples that can be attributed to the α′ transition. This transition is possible due to motions resulting from crystallites of different length from those giving rise to the α transition.[8]

The mechanical properties were also studied through the stress/strain curves using an Universal Test Machine (Wolpert TSS) at 50m/min and room temperature. The results were the average of at least 3 test for each sample. We compared the elastic moduli and the yield points but we do not evaluated elongation at break since some samples at higher strains have slipped between the grips.

Figure 5 shows the stress/strain experiments of a EP copolymer and three EPH terpolymers with a very low amount of propylene (0.2–0.8 mol%). The copolymer presented the highest elastic modulus and a marked yield point. The presence of 1-hexene from 1.3 to 2.2mol% in the terpolymers caused a significant decrease in the modulus and a less defined yield point, giving a material more elastomeric. The differences on the amount of 1-hexene and percentage of crystallinity (from 32 to 37%) in the terpolymers is too small to give significant differences among the terpolymer stress/strain curves.

Figure 6 shows the same behavior. The incorporation of an amount of 1-hexene of 1.3 and 2.3mol% causes a strong depression in the crystallinity compared to the EP copolymer and consequently in the mechanical properties, converting a rigid material in a more elastomeric one. The terpolymers with very close amounts of propylene (1.1 and 1.5 mol%) and amounts of 1-hexene of 1.3 and 2.3 mol% present similar stress/stress curves, showing that the increase of butyl branches from 1.3 and 2.3 mol% and increase of crystallinity from 30 to 35% in the terpolymer is not significant to the mechanical properties.

Figure 7 shows the stress/strain curves of terpolymers with similar amount of 1-hexene and different amounts of propylene.

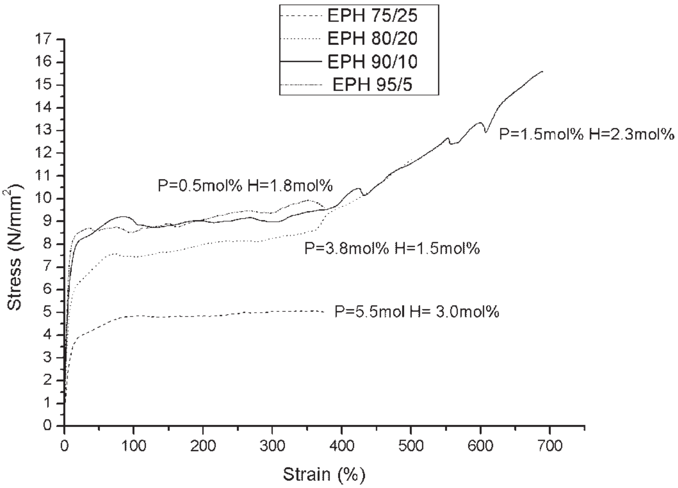

Figure 10.

Mechanical properties of the EPH terpolymers obtained with same catalyst systems: $Cp_2ZrCl_2/MAO/SiO_2$ using the different E/P ratios [H] = 0.176 M in the feed.

It can be seen that the presence of propylene from 0.2 mol% to 3.0 mol% produces a stronger decrease in the modulus than it was produced by 1-hexene at similar propylene amounts. Mechanical properties seems more affected by the amount of propylene than by the amount of 1-hexene. This behavior is more evident in Figure 8 where it can be seen a clear difference between the two terpolymers with propylene amount of 1.8 mol% and amounts of 1-hexene of 0.5 and 2.6 mol%. Figure 9 also shows the influence of the propylene content in the stress/strain curves. The same samples studied in the dynamic mechanical properties show an inverse behavior: the sample with less propylene content (0.2 mol%) and higher 1-hexene content (2.2 mol%) needs a higher stress for the same deformation than the sample with more propylene (2.9 mol%) and inferior 1-hexene content (0.7 mol%). Mechanical properties are more influenced by propylene and the dynamic mechanical properties by 1-hexene. The difference is that the first ones measure the crystalline phase and the second one the amorphous phase.

Terpolymers obtained with the same catalytic system and different E/P ratios show different moduli depending mainly on the propylene content (Fig. 9).

Differences in molecular weights showed to be less significant in the mechanical properties than differences in the amount of comonomers and crystallinity.

Conclusion

Metallocenes are excellent catalytic systems to obtain ethylene-propylene-α-olefin terpolymers. Metallocenes with bridge such as $Et[Ind]_2ZrCl_2$ incorporates more comonomers than that without bridge as Cp_2ZrCl_2. On the other hand, the latter, homogeneous and supported systems, affords higher catalytic activities than that with bridge. This systems allows to obtain random terpolymers of ethylene with propylene and 1-hexene. These materials have thermoplastic or elastomeric behavior depending on the propylene and 1-hexene incorporations. 1-hexene showed to exert more influence on the dynamic mechanical behavior of the terpolymers then propylene and the amount of propylene a stronger influence on the stress/strain behavior curves, probably due to the fact that the methyl branch forms part of the crystalline lattice and butyl branches are part of the amorphous phase.

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