Influence of the Type and the Comonomer Contents on the Mechanical Behavior of Ethylene/α-Olefin Copolymers

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ABSTRACT: The influences of the type and concentration of α-olefin (1-hexene, 1-octene, 1-decene, 1-octadecene, 4-methyl-1-pentene) on the mechanical behavior and crystallinity degree of some ethylene/α-olefin copolymers obtained by metallocene catalysts were studied by means of stress/strain experiments. The crystallinity degree of these copolymers has been determined by X-ray measurements. It has been observed that the copolymers show less resistance to strain as the comonomer content increases and the crystallinity decreases. Most of the studied copolymers exhibit a significant increase in the crystallinity level after the stress/strain experiments. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1194–1200, 1999

Key words: ethylene/α-olefin copolymers; crystallinity; stress/strain experiments

INTRODUCTION

In general, the physical properties of semicrystalline polymers, such as polyethylene, depend on a set of different variables, for example, molecular weight and molecular structure. In the case of ethylene/α-olefin copolymers, the α-olefin content plays an important role on these properties.[1,2] The presence of short branches disturbs the crystallization kinetics, giving rise to copolymers with different properties. In our previous works,[3–5] it was demonstrated that the degree of crystallinity and the melting point of the ethylene/α-olefin copolymers decrease as the comonomer content is increased.

Many studies are found in the literature about the effect of branching on the crystallization behavior and properties of ethylene/α-olefin copolymers.[1,6–8] In these cases, it is generally accepted that the methyl branches are included in the crystalline lattice, but branches higher than propyl are not able to enter the crystalline phase, creating a thin interphase inside the amorphous domain. This intermediary region presents some organization and some crystallinity. The tendency for segregation of short branches depends on their size, and the interfacial layer is extended with an increase in the contents of short branches.[8,9]

The concentration of the comonomer unit influences the mechanical behavior of the ethylene/α-olefin copolymers. The Young modulus of these copolymers depends on crystallinity, increasing with it. Some authors pointed out that the distribution and type of branch have only small effects on the modulus of copolymers with aliphatic branches, although considerable variations with increasing the amount of the branches have been observed.[1,10] Several studies report[10,11] that ethylene copolymers exhibit high resistance to strain, upholding to large elongations as the crystallinity increases.

The degree of crystallinity also influences the yield point of the copolymers. Some authors suggest that the dependence of the yield stress on crystallinity could be related to structural changes of the crystallites and associated regions at the yield point.[11,12] A mechanism to explain these changes was proposed by Flory and Yoon[13] and is related to the partial-melting recrystallization process involved in the deformation process. This partial melting consists of the fusion of less perfect crystallites that recrystallize in the draw direction. The energy for partial melting comes from the overall stress being concentrated on the less-perfect crystallites.[10]

When an isotropic polymer is subjected to an external stress, it generally undergoes a structural rearrangement or orientation. In amorphous polymers, the randomly coiled chains are rearranged and in the crystalline polymers the crystallites can be reoriented or completely rearranged. An oriented recrystallization may be induced by the applied stress.[14]

Being stretched to a critical limit, a crystalline polymer undergoes structural changes that improve the crystalline organization, as in the alignment of polymer chains (or branches). The crystallinity increases with the elongation, indicating a recrystallization of the chains pulled out of the crystalline region.[15] The orientation has effects on the physical properties, such as tensile strength and stiffness.

The study of the mechanical properties of ethylene/α-olefin copolymers is very important for finding its limiting performance and establishing the best relationships between molecular structure and mechanical behavior.

EXPERIMENTAL

Copolymers based on ethylene with different concentrations of 1-hexene, 1-octene, 1-decene, 1-octadecene, and 4-methyl-1-pentene obtained by metallocene catalysts (Et[Ind]$_2$ZrCl$_2$/Methylaluminoxane [MAO])[3,4] were melt-pressed to obtain thin films at temperatures of 30 to 35°C above their melting point. 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 gage length, 10-mm width, and thickness in the range of 0.20 to 0.30 mm.

X-ray measurements were carried out in a Siemens D-500 diffractometer. The data were collected in intervals of 0.05 degrees, between 4 and 50 degrees. A copolymer sample was used before and after the stress/strain measurements.

The molecular weight of the copolymers was determined by gel permeation chromatography in a Waters 150 CV-plus System, equipped with an optic differential refractometer, 150 C model. A set of three columns, Styragel HT type (HT3, HT4, HT6), was used. The analyses were performed in 1,2,4-trichlorobenzene at 140°C and 1.0 mL/min. The columns were calibrated with narrow molar mass distribution standards of polystyrene and polyethylene.

Differential Scanning Calorimetry (DSC) measurements were performed on a Polymer Laboratories DSC instrument under N$_2$ atmosphere. The samples were heated from 40 to 150°C and cooled down to 40°C at a heating/cooling rate of 10°C/min to determine the melting temperature. The melting temperature values (T_m) and the heat of fusion (ΔH_f) were taken from the second heating curve. The degree of crystallinity was calculated from ΔH_f, using the equation $X_c = \Delta H_f \times 100/64.5$.[16]

RESULTS AND DISCUSSION

Table I shows the properties of some ethylene/α-olefins copolymers. As was mentioned earlier, the crystallinity and the melting point depend on the amount of incorporated α-olefin: both decrease with the increase in the α-olefin content.[2–4]

It is known that copolymers of ethylene and α-olefins with long chains, such as 1-octadecene, might show a different behavior from that usually found for ethylene/short α-olefins copolymers.[7,17] It is accepted that long branches may participate in the crystallization process, favoring the crystallinity. Also, it is possible that long branches can crystallize, forming crystallites with different sizes when compared with the main crystallizable chain.[17] In the case of ethylene/1-octadecene copolymers, several DSC thermograms exhibit the presence of more than one endotherm, indicating that the copolymers have more than one melting temperature (Table I). This behavior has been observed, especially for the copolymer with 5.1% of 1-octadecene and indicates the presence of crystals with different sizes.

It is also important to point out the differences between the crystallinity values obtained by DSC

Table I   Properties of Ethylene/α-Olefins Copolymers

| α-Olefin (% M) | Melting Point (°C) | Crystallinity Values (%) | | | M_w | M_w/M_n |
		DSC	X-ray Before[a]	After[b]		
			Ethylene/1-Hexene			
5.6	99	33	39	39	90,300	1.9
6.2	83	17	30	31	47,500	2.5
11.0	60	9	22	23	60,700	2.0
15.8	56	4	0	0	46,200	1.5
			Ethylene/1-Octene			
2.3	111	43	46	51	94,200	1.9
5.0	98	29	33	33	49,500	2.7
8.2	83	14	18	60	45,200	2.0
10.3	73	5	15	38	41,800	2.0
			Ethylene/1-Decene			
<1.0	119	52	57	56	n.d.[d]	n.d.
1.6	114	46	53	54	n.d.	n.d.
2.1	113	45	51	54	97,000	1.6
10.8	86	9	19	46	54,200	1.7
15.2	48	1	0	0	n.d.	n.d.
			Ethylene/4-Methyl-1-Pentene			
3.7	108	40	41	82	n.d.	n.d.
5.1	92	20	23	56	34,100	1.7
11.4	69	14	—	54	27,900	1.7
14.0	60	10	n.d.	n.d.	n.d.	n.d.
			Ethylene/1-Octadecene			
1.8	120	41	62	89	152,000	2.5
2.4	115	36	62	n.d.	143,000	2.4
3.4	112	21	63	90	n.d.	n.d.
5.1	90/14[c]	40(27 + 13)[c]	45	85	97,000	2.1

[a] Crystallinity values *before* the stress/strain experiments.
[b] Crystallinity values *after* the stress/strain experiments.
[c] Two melting points observed and the crystallinity values at these regions.
[d] Not determined.

and X-ray measurements, where in general, the values from X-ray were larger than those from DSC. These differences are reasonable because the two techniques take into account different aspects of the phase structures. Values from DSC are based on the enthalpy of fusion (a property related to the crystallinity), whereas values from X-ray measurements directly determine the crystalline structure. Both methods are subjected to uncertainties, especially due to the arbitrary definition of the baseline or the limits between amorphous and crystalline phases. These differences are more evident for ethylene/1-octadecene copolymers.

The crystallinity values have also been obtained by X-ray diffraction (Table I) for the samples after the stress/strain measurements. These measurements have been undertaken to verify whether the copolymers undergo an oriented recrystallization induced by the applied stress. Based on these results, no obvious differences have been detected in the crystallinity values between the two samples (*before* and *after*) for ethylene/1-hexene copolymers. Ethylene/1-octene and ethylene/1-decene copolymers exhibit an increase in the crystallinity degree after the stress/strain measurements for samples with higher comonomer contents (>8%). Copolymers with differences in the degree of crystallinity after the stress/strain experiments possess an initial degree of crystallinity lower than 20%. Copolymers with larger initial values present the same crystallinity after the stress/strain experiments. The ethylene/4-methyl-1-pentene and ethylene/1-octadecene possess higher crystallinity after the
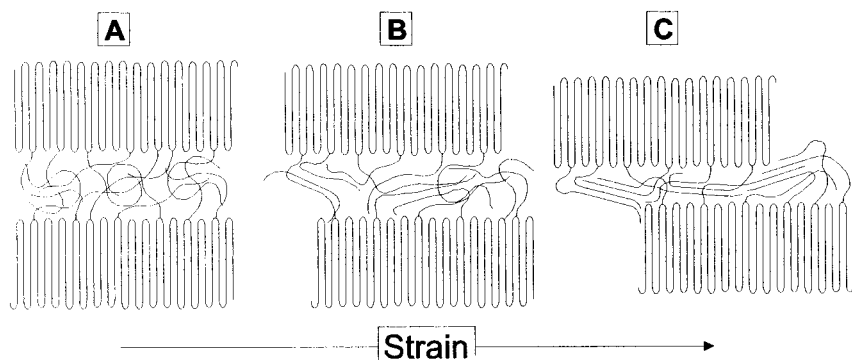
Figure 1 Schematic representation of the stress-induced orientation at the interface.

stress/strain experiments for all copolymers studied.

It has been reported that the crystallinity changes only slightly during the drawing for copolymers with high crystallinity (such as the copolymers of E/1-O and E/1-D with low comonomer content).[14] On the other hand, if the crystallinity of the sample before drawing is low, it can be induced by the drawing. For copolymers with high comonomer content, the branches probably are excluded from the crystalline lattice forming an interfacial region between the crystalline and amorphous phases. This interfacial region may present some ordering retained from the crystalline phase.[2] As stress is applied, some strain-induced crystallization probably occurs in these uncrystallized or partially crystallized chains (branches). This effect is more pronounced for the ethylene/4-methyl-pentene copolymers that show an accentuated increase in the crystallinity for all copolymers studied under stress.

The general model accepted for the polyolefin crystallization is the folded chain lamella. Methyl side chains may be incorporated into lamella, but medium and long chains are excluded. In copolymers with higher comonomer content, the average distance between two side chains might influence the lamellar thickness.[8,18] Thus, copolymers with low crystallinity and long side chains are able to develop additional crystallinity when submitted to strain. Such behavior arises from the shear at the interface, allowing the reordering and crystallization of the side chains, as depicted in Figure 1.

Figures 2, 3, 4, 5, and 6 show the stress versus strain curves for several ethylene/α-olefin copolymers with different comonomer contents. Evidently, all the copolymers exhibit smaller stress values as the comonomer content increases (and crystallinity decreases), indicating that the mechanical response of semicrystalline polymers is really determined by the sample crystallinity. It
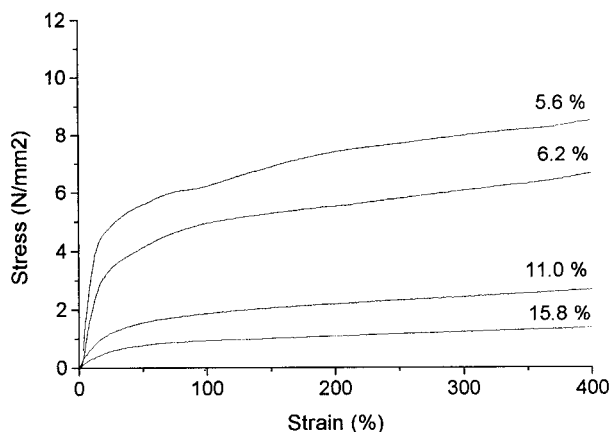
Figure 2 Stress/strain curves of ethylene/1-hexene copolymers with different comonomer contents.
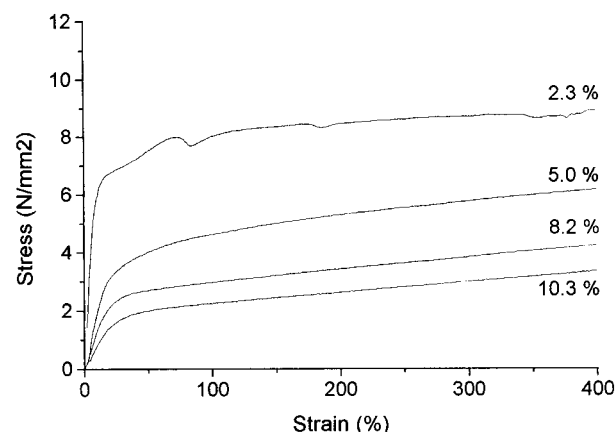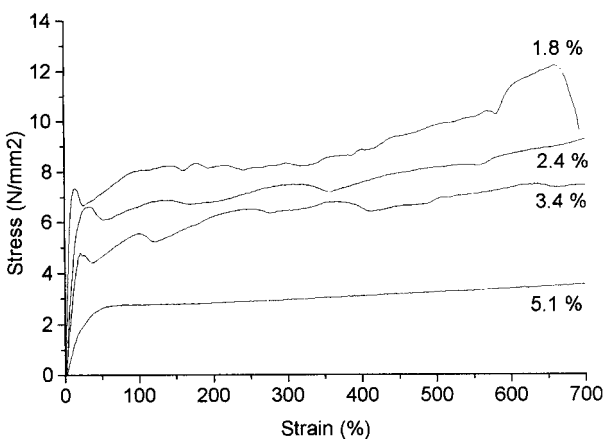

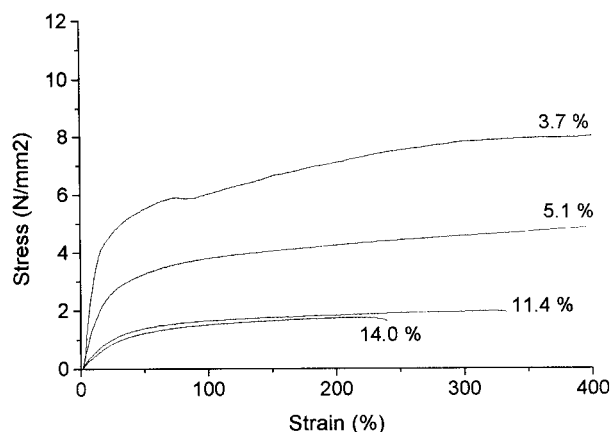**Figure 3** Stress/strain curves of ethylene/1-octene copolymers with different comonomer contents.
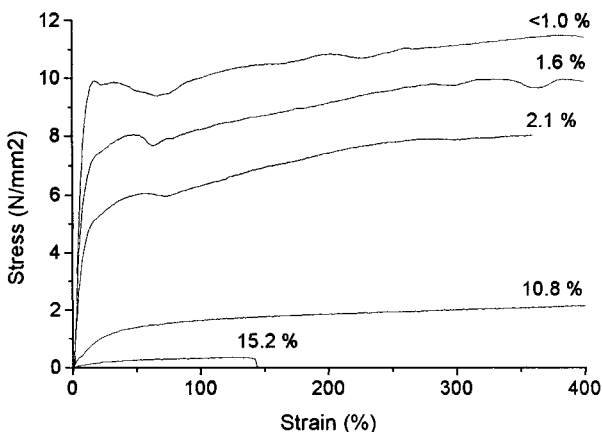
Figure 4 Stress/strain curves of ethylene/1-decene copolymers with different comonomer contents.

Figure 6 Stress/strain curves of ethylene/4-methyl-1-pentene copolymers with different comonomer contents.

is also possible to verify that the copolymers with larger comonomer contents (>6%) show stress/strain curves similar to those commonly obtained for elastomeric materials. The plots do not represent the full stress/strain experiment, but only up to 400% of strain. Most of the samples have been elongated up to more than 900%, but since some samples at higher strains have slipped between the grips, it was impossible to evaluate some parameters such as the strain hardening and the elongation at break.

Another important point is the difference observed in the yield region of the copolymers in function of crystallinity. It has been reported[12,19] that the yield region becomes more diffuse as the degree of crystallinity decreases. In Figures 2, 3, 4, 5, and 6, the yield point can be clearly observed for copolymers with less than 5% of α-olefin con-

tents. The copolymers with lower α-olefin contents have higher yield stress. Figure 7 shows the variation of the yield stress with the comonomer contents for several ethylene/1-decene and ethylene/1-octadecene copolymers. It seems that the yield stress does not depend on the type of comonomer, but on the comonomer contents, decreasing with the comonomer contents in the copolymers.

The necking of the samples has been observed for all copolymers in the stress/strain measurements. However, in the case of ethylene/1-octadecene copolymers, two or more necks were formed, as can be observed in Figure 5 for samples with less than 5% of comonomer. Such behavior might

Figure 5 Stress/strain curves of ethylene/1-octadecene copolymers with different comonomer contents.
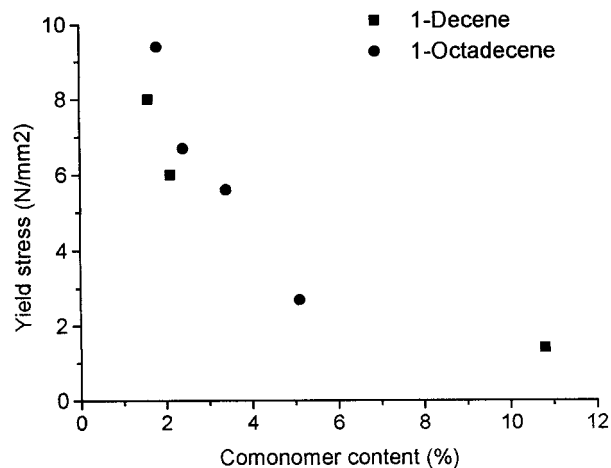
Figure 7 Yield stress versus comonomer content (%) for ethylene/1-decene and ethylene/1-octadecene copolymers.
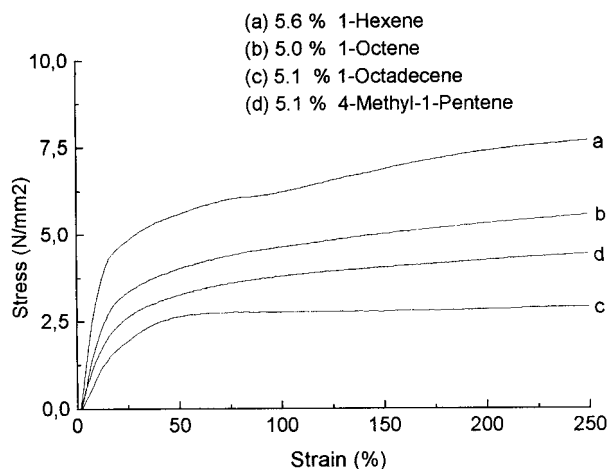
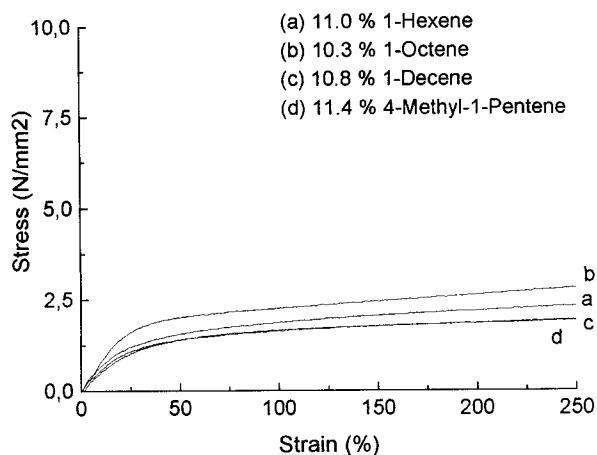**Figure 8** Stress/strain curves for ethylene/α-olefin copolymers with 5% comonomer contents.

Figure 9 Stress/strain curves for ethylene/α-olefin copolymers with 10% comonomer contents.

be related to chemical and/or morphological heterogeneities or to the effect of strain dynamics on the recrystallization possibilities.

The stress/strain behavior of the copolymers is also affected by the molecular weight and molecular weight distribution of the copolymers. For the studied ethylene/α-olefin copolymers, the molecular weight (M_w) decreases with the increase of comonomer contents. In general, differences observed in the molecular weights are larger for the copolymers with smaller comonomer contents. Most of the copolymers exhibit molecular weight distributions of approximately 2.0. The ethylene/1-octadecene copolymers present larger molecular weights when compared to the other ethylene/α-olefin copolymers (Table I), but their molecular weights have been determined using a calibration curve for linear polyethylene.

Another interesting point is the influence of the size and type of branch on the stress/strain behavior. Figure 8 illustrates the curves for ethylene copolymers with about 5% of comonomer contents. Comparing the curves to those for linear comonomers (1-hexene, 1-octene, and 1-octadecene), one might conclude that longer comonomers have lower resistance to strain. The ethylene/4-methyl-1-pentene copolymer shows an intermediate behavior between the ethylene/1-octene and ethylene/1-octadecene copolymers. The isopropyl group in the branch is highly efficient in decreasing the crystallinity and, as a consequence, the resistance to strain. Figures 9 and 10 show similar curves obtained for the same copolymers with higher comonomer contents: 10 and 15%, respectively.

Comparing Figures 8, 9, and 10, it becomes evident that as the comonomer contents increase, the samples do not obey the same order with respect to tensile stress. At higher comonomer contents (10 and 15%), the differences between the stress values are very small and it is difficult to relate it to the comonomer structure and size. At smaller comonomer contents (5%), the observed differences are more evident, indicating that for small comonomer contents, the type of comonomer has some influence on the resistance to strain. At larger comonomer contents (10 and 15%), no significant differences in the stress values have been found, indicating that the type of comonomer does not have a significant effect at these concentrations (10 and 15%).
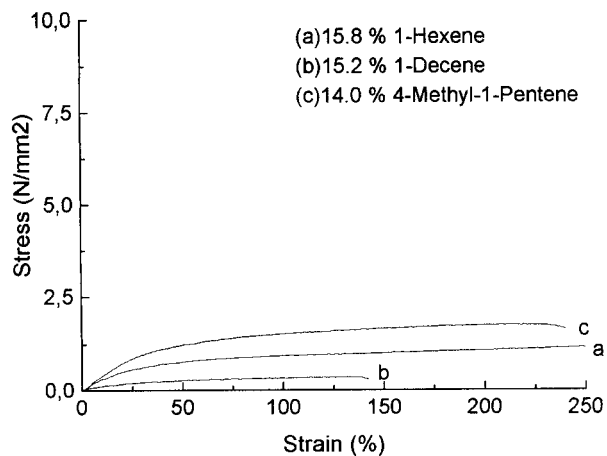
Figure 10 Stress/strain curves for ethylene/α-olefin copolymers with 15% comonomer contents.
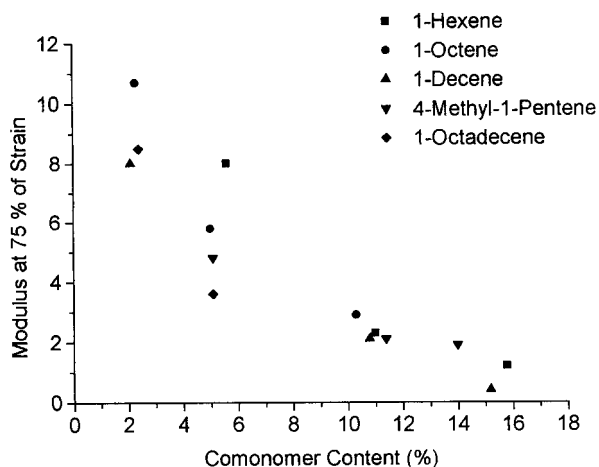
Figure 11   Modulus at 75% strain versus comonomer contents (%) for ethylene/α-olefin copolymers.

Figure 11 presents the variation of the modulus (at 75% of strain) with the type of comonomer. At smaller comonomer contents, the copolymers exhibit different moduli, probably influenced by the size of comonomer (1-hexene > 1-octene > 1-decene). At larger comonomer contents (>10%), the moduli are quite similar for all the copolymers. These results confirm the earlier observations that indicate that the effect of the type of comonomer is more pronounced for small comonomer contents.

CONCLUSIONS

The main factor affecting the stress/strain behavior of the investigated ethylene/α-olefin copolymers is the degree of crystallinity. In general, the higher the crystallinity, the higher the yield stress and the resistance to strain of these copolymers. Since the degree of crystallinity is directly related to the comonomer contents (it decreases as the comonomer content increases), one might conclude that there is a strong dependence of the mechanical properties on the concentration of comonomer in the copolymers.

The type of comonomer scarcely affects the mechanical behavior. We have observed that for comonomer contents of 5%, some differences in the stress values occur according to the size of the branch, which can be related to the differences in crystallinity. Conversely, for larger comonomer contents (10 and 15%), the size of the branch does not influence the mechanical behavior, probably because, at these comonomer contents, the degree of crystallinity is so small that its influence on the mechanical properties can be neglected.

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