Characterization of Metallocene Ethylene-1-Octene Copolymers with High Comonomer Content Cross-linked by Dicumyl Peroxide or β-Radiation

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ABSTRACT: Two metallocene ethylene-1-octene copolymers differing in comonomer content were cross-linked either by dicumyl peroxide (DCP) or β-radiation with doses ranging from 0.5 to 4% DCP and 25 to 200 kGy, respectively. The effect of cross-linking on the crystalline morphology was analyzed by differential scanning calorimetry (DSC). Slight alterations in the crystalline structure were found, which were more severe in the case of peroxi modification. Through infrared spectroscopy (FTIR analysis), oxidation during the cross-linking process was detected on the DCP cross-linked samples, while β-irradiated samples do not exhibited significant degrees of oxidation. The state of cure was studied following the changes in the rheological properties in small-amplitude oscillatory shear mode, and the evolution of the molecular weight and molecular weight distribution through size exclusion chromatography. Irradiation doses below 200 kGy increased the molecular weight and branching of both copolymers but were not sufficient to reach gelation. All the peroxide modified samples resulted in a post-gel condition. Optimal mechanical properties were obtained with concentration of about 1% DCP. At higher doses, scission reactions diminish the tensile strength and the elongation at break. When polymers with equivalent amounts of gel fraction obtained by the two modification procedures studied in this work are compared, higher tensile strength and elongation at break are obtained with irradiation. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2691–2700, 2009

Key words: cross-linking; electron beam irradiation; ethylene-1-octene copolymers; metallocene; peroxide

INTRODUCTION

The development of metallocene catalysts in the field of polyolefins permits the production of new ethylene copolymers with very low density that constitutes a unique class of thermoplastic elastomers.[1,2] These polymers have a potentially wide range of applications and are of special interest for the automotive industry. Most of the uses in this field require a good balance of mechanical properties at high temperatures. Cross-linking is then required to expand the range of thermal service for these materials.[3–6]

Ethylene-1-octene copolymers belong to the group of ethylene-α-olefin copolymers synthesized for elastomeric applications. They can be obtained with homogeneous comonomer distribution, different comonomer concentration, and narrow polydispersities, allowing a good control of the chain microstructure. This provides a unique opportunity to model structure-property relationships. The influence of comonomer type and content on a wide variety of aspects including structure, morphology, crystallinity, crystallization, and melting behavior has been covered by a large number of investigations.[6–19] But there is a lack of studies on the properties of these copolymers after being cross-linked.

Saturated polymers such as ethylene-1-octene copolymers can be cross-linked by β-irradiation[20–22] or high temperature peroxide decomposition.[23,24] Irradiation is usually applied to finished parts at room temperature. Cross-linking with peroxides requires high temperatures and it is performed on the molten state, usually in the last processing step.

This work is focused on the characterization of metallocene ethylene-1-octene copolymers with high comonomer content cross-linked by dicumyl peroxide (DCP) and β-radiation.

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TABLE I
Characteristics from Supplier and Molecular Weights of Commercial Metallocene Ethylene-1-Octene Copolymers

Copolymer	Comonomer content (Mol %)	Comonomer 1-octene (wt %)	Density (g/cm^3) ASTM D-792	Melt flow index (dg/min) ASTM D-1238	Molecular weights			
					M_n	M_w	M_w/M_n	Detector
EG8400	14	40	0.870	30	22300	51900	2.33	RI
					49200	69100	1.40	MALLS
EG8411	10	33	0.880	18	26300	54100	2.17	RI
					40700	64600	1.59	MALLS

EXPERIMENTAL

The materials used were two metallocene ethylene-1-octene grades supplied by DuPont-Dow Elastomers, whose characteristics are shown in Table I. The organic peroxide used was DCP (99% purity) supplied by Atofina. Previous to use, it was recrystallized from methanol.

Peroxide cross-linking was induced by previously mixing different amounts of DCP (0.5–10 phr) with the ethylene-octene copolymers in a Leistritz corrotating twin-screw extruder at 85°C, 55 rpm, and 2 kg/h of mass flow rate. After mixing, compression molded samples were cross-linked at 190°C under a pressure of 30 MPa.

β-irradiated copolymers were obtained by the following procedure. Compression molded samples of the virgin copolymers were irradiated in air by an electron beam accelerator (model Rhodotron TT200, 10 MeV) with irradiation doses ranging from 25 to 200 kGy. The irradiation procedure was carried out in steps up to 50 kGy to avoid an excessive heat generation within the polymer. Therefore, the irradiation of samples with 25 and 50 kGy was carried out in one single step whereas samples irradiated up to 100 and 200 kGy required second and fourth steps, respectively. No thermal treatment was performed on the samples after irradiation.

The changes in molecular weight and molecular weight distribution due to cross-linking were followed by size exclusion chromatography (SEC) using a Waters 150-C ALP/GPC equipped with a standard refractive index (RI) detector in series with a Multi-Angle Laser Light Scattering (MALLS) spectrophotometer Dawn DSP (Wyatt Tech), laser He-Ne (632.8 nm). A set of three (20 μm PL-GEL MIXED-A) columns from Polymer Labs was used with 1,2,4-trichlorobenzene (TCB) at 135°C as solvent with 1 mL/min flow. The apparent molecular weights of the polymers were estimated following the standard calibration procedure using monodisperse polystyrene samples and the corresponding Mark–Howink coefficients for polystyrene and linear polyethylene.[25,26]

Fourier Transform Infrared (FTIR) analysis of the original polymers and the cross-linked materials was carried out on a Bomem (Hartmann and Braun, ABB, Quebec, Canada) Model NB-150 mounted on a Golden Gate ATR accessory, with a 4/cm resolution and 64 scans. Samples were 2 mm of thickness.

Differential scanning calorimetry (DSC) scans were recorded on a Mettler Toledo (Greifensee, Switzerland) DSC 821/400 at a heating rate of 10°C/min. The rheological characterization was carried out in small-amplitude oscillatory shear mode using a rotational rheometer from Rheometrics (Rheometric Dynamic Analyzer RDA-II). The tests were performed using parallel plates 25 mm in diameter, at frequencies between 5×10^{-2} and 5×10^{2} rad/s. Experiments in the rheometer were carried out at temperatures ranging from 30 to 90°C. All tests were done at small strains to assure the linearity of the dynamic responses. Several of the series of frequency sweeps were repeated twice with the same sample. Excellent agreement between the results was found in all cases, indicating that no measurable degradation occurred during the rheological tests.

Finally, the gel content of the cross-linked samples was determined in boiling xylene according to the ASTM D2765-95. Tensile tests were performed according to the UNE-EN ISO 37 standard methods.

RESULTS AND DISCUSSION

Characterization of the original polymers

The molecular characterization of the original copolymers by SEC with RI detector and MALLS is reported in Table I. Values of M_n and M_w/M_n obtained with MALLS are distorted with respect to those of the RI detector because of the lack of ability of MALLS to evaluate the lower molecular weight side of the chromatograms. Irrespective of these differences, the results show that both copolymers have a narrow molecular weight distribution and similar weight average molecular weights.

Through the FTIR characterization, the presence of unsaturations, such us the vinyl-ending groups, can be detected and quantified. The unsaturations content of both polymers was explored using the peak at 908/cm associated to the double bonds from the vinyl-ending groups. This kind of unsaturations is of importance because they are known to enhance the efficiency of the cross-linking process.[27] The results from these measurements indicated that the bands

TABLE II
Thermal Properties DCP Cross-Linked and β-Irradiated Copolymers

Copolymer	DCP amount (phr)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	Irradiation dose (kGy)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
EG8400	0.0	64	49	49	49	0	64	49	49	49
	0.5	63	48	45	47	25	65	49	49	46
	1.0	62	47	44	46	50	64	48	48	46
	2.0	61	48	44	45	100	65	47	46	44
	4.0	58	47	37	42	200	63	48	45	44
EG8411	0.0	77	64	55	64	0	77	64	55	64
	0.5	74	61	57	63	25	76	65	55	63
	1.0	72	61	54	61	50	76	63	55	60
	2.0	70	57	52	57	100	77	61	54	60
	4.0	69	58	45	55	200	74	62	54	60

corresponding to terminal insaturations were almost undetectable indicating that very low content of vinyl terminal groups were present in the original polymers.

The melting behavior of both materials was studied by DSC. They exhibited the typical behavior of ethylene-octene copolymers with high content of hexyl branches (48 and 71 branches per 1000 backbone carbon atoms for EG8411 and EG8400, respectively).[19,28] On cooling from the melt, a broad melting range was observed up to temperatures in the range of −20 to −40°C. The low values of the melting enthalpy (ΔH_m), which are displayed in Table II, indicate that both copolymers have also very low degree of crystallinity due to the high level of short chain branching (SCB). Because of its higher content in 1-octene, *EG8400* exhibits lower values of ΔH_m and location of the maximum peaks for melting (T_m) and crystallization (T_c) at lower temperatures on the thermograms.

The reversibility of the crystallization and melting processes in the copolymers was investigated by looking at the evolution of the degree of crystallinity as a function of temperature [$\chi_c(T)$] by cooling the molten polymers from the melt at constant rate and then reheating each sample at the same rate that it was cooled up to well beyond T_m. For this purpose, after erasing the previous thermal history by keeping the copolymers at 150°C for 5 min, they were cooled at a constant rate (10°C/min) up to −30°C and then re-heated at the same rate up to complete melting. The evolution of the degree of crystallinity as a function of temperature was obtained through the progress of the partial areas of the DSC thermograms converted into degrees of crystallinity through the appropriate scaling factors. For this purpose, the value of the heat of fusion of orthorhombic polyethylene (288.4 J/g) was used, irrespectively of the region of the thermogram analyzed. The comparison of the curves in Figure 1 clearly indicates that the crystallinities obtained from the heating and the cooling traces are identical at low temperatures, and depart significantly from each other at higher temperatures. Consequently, two regions of temperature dependence of the crystallinity are distinctive in these polymers: a high temperature region that exhibits a significant degree of hysteresis, and a lower temperature region with a remarkably reversible behavior. Alizadeh et al.[28] have made similar observations on ethylene-octene copolymers showing that the hysteresis region decreases progressively with increasing comonomer content. The transition temperature between these two regions marks the crossover from two different crystalline morphologies. The high temperature region is characteristic of a nucleation controlled chain-folded lamellar growth process that is cooling-rate dependent. Here lamellar crystals melt at temperatures higher than the temperatures at which they were generated.[28,29] Whereas, the low temperature region is not associated with a lamellar morphology, and thus, it is cooling rate independent. This reversible region

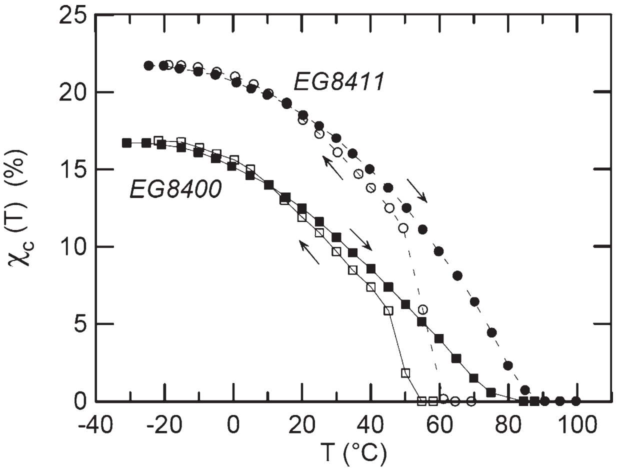

Figure 1 Degree of crystallinity as a function of temperature for the original ethylene-1-octene copolymers in cooling and heating processes. (■) *EG8400*, heating; (□) *EG8400*, cooling; (●) *EG8411*, heating; (○) *EG8411*, cooling.

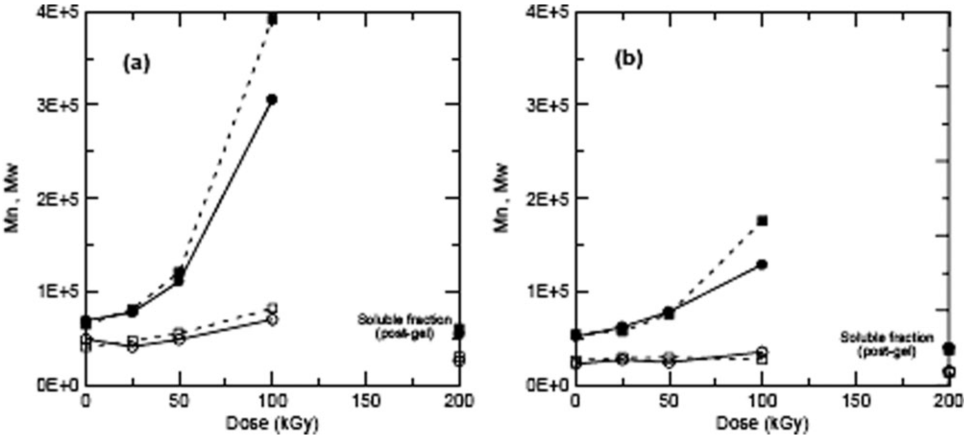

Figure 2 M_w and M_n for β-irradiated copolymers. (a) MALLS; (b) RI detector. (○) M_n and (●) M_w for *EG8400* (solid lines); (□) M_n and (■) M_w for *EG8411* (dashed lines).

corresponds to low size crystallites, whose thicknesses and lateral dimensions are much smaller than those of chain-folded lamellar crystals. The typical morphology of this region exhibits bundle-like micellar crystals.[2,30]

Small amplitude oscillatory shear experiments performed on the virgin resins at 90°C allow to construct Van Gurp-Palmen plots of phase angle δ versus complex modulus G* (not shown) that correlate very well with the extensive rheological characterization performed by García-Franco et al.[31] on different ethylene-octene copolymers of equivalent octene content. The evolution of G′ versus frequency at 90°C [shown in Fig. 4(c,d)] for *EG8411* gives consistently higher values than those of *EG8400* irrespective of their similar weight average molecular weight values. This is a direct consequence of the lower content of short hexene chains in EG8411.

Cross-linked samples characterization

Molecular characterization

The changes in the molecular weight and molecular weight distribution of both copolymers due to the cross-linking processes by β-radiation and DCP were analyzed by SEC combined with MALLS. When radiation was used to modify the original copolymers, only those irradiated with 200 kGy exhibited an insoluble phase. Therefore, the samples irradiated between 25 and 100 kGy belong to the pre-gel region. As expected, chain-linking reactions prevailed over the chain scission reactions. This resulted in a net rise of M_w and M_n for both copolymers with increasing doses of radiation.

Figure 2 illustrates these changes for the β-irradiated copolymers. A sharp increase in the values of M_w and M_n for both irradiated copolymers is observed irrespective of the detector employed in the estimation of the molecular weights. Obviously, the values of M_w and M_n determined by MALLS are higher than the values obtained with the RI detector, because the former detector is more sensitive to molecules of higher size. Moreover, the divergence between M_w values measured by MALLS and RI detectors tends to increase as the degree of chain branching induced by the cross-linking process becomes more important at doses close to those of the gel point. This is a consequence of the lower hydrodynamic volume, characteristic of highly branched molecules formed in the vicinity of this point that are computed with the RI detector as linear molecules of lower molecular weight.

The results of these measurements show that the efficiency of the cross-linking reaction was higher for *EG8411* because at equivalent doses of irradiation, higher molecular weights were obtained. This is evident in the figure for the results at 100 kGy. The molecular structure of the *EG8411*, that contains a lower content of 1-octene comonomers in the main chain, is the most probable reason for this behavior. The presence of tertiary carbons favors scission reactions, which, in turn, reduce the efficiency of the cross-linking reactions on the *EG8400* copolymer.

Samples irradiated above the gel point with 200 kGy required an extraction process in hot xylene to obtain the gel fraction, which has been later injected in the chromatograph. The higher efficiency of the cross-linking process on the *EG8411* was also confirmed through the analysis of the amount of gel fraction obtained from the samples irradiated with 200 kG, because a gel fraction of 58% was measured for the irradiated *EG8400* whereas 68% gel was obtained from *EG8411*. The soluble fraction extracted from the gel has been later injected in the chromatograph to evaluate the changes on the molecular weight. At this dose, the measured values of M_w and M_n from the extracted soluble fractions were

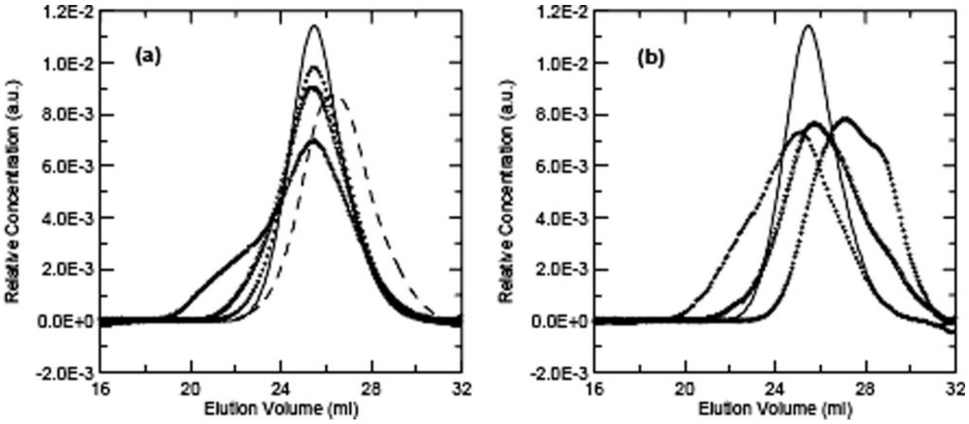

Figure 3 Molecular weight distributions by SEC (RI detector) of (a) β-irradiated *EG8411* copolymers. Solid line: neat polymer, (●) 25 kGy, (▽) 50 kGy, (+) 100 kGy, and dashed line: 200 kGy. (b) DCP cross-linked *EG8411* copolymers. Solid line: neat polymer, (●) 0.5% DCP, (▽) 1% DCP, and (+) 2% DCP.

slightly lower than those corresponding for the original copolymers. Two factors are responsible for this fact: (1) in the post-gel region high molecular weight chains are preferentially incorporated to the gel fraction because of their higher mass, they have more probability to be cross-linked and attached to the gel; (2) chain scission due to the high tertiary carbon content of these copolymers. The existence of scission reactions is clearly established through the observation of the SEC traces of the irradiated samples. Figure 3(a) shows as an example, the elution curves of the original *EG8411* copolymer and those of the same polymer irradiated with increasing doses of β-irradiation. With doses up to 100 kGy, a gradual widening of the high molecular side of the elution curve is clearly observed because of the formation of high size molecules produced in the chain-linking process. A slight displacement, that is not clearly observed at the scale of the plot, attributed to scission reactions, is also noticeable in the low molecular weight side. This displacement towards low molecular weights is unmistakably measurable when the analysis is performed in the extractable fraction of the sample irradiated with 200 kGy. Here, the SEC curve is totally displaced towards much higher elution volumes indicating that, during the irradiation process, a considerable amount of low molecular weight molecules have been generated through scission reactions.

All the copolymers treated with different concentrations of DCP resulted in highly cross-linked post-gelled materials. Figure 3(b) shows the evolution of the SEC chromatograms for the different samples obtained from *EG8411* with increasing amounts of peroxide. The curve corresponding to this polymer cross-linked with 4% of DCP is not shown because the soluble fraction obtained in this case was so slight that it was not enough to be injected in the chromatograph. The chromatogram obtained from the copolymer treated with the lower peroxide dose of 0.5% DCP correspond to its sol fraction in the vicinity of the gel point. It exhibits, as in the case of those already discussed for the irradiated samples, a significant shift of the elution curve towards lower elution volumes. This reflects the notable increase on the molecular weight and molecular weight distribution because of cross-linking. The rest of the elution curves show a continuous displacement towards higher elution volumes with increasing doses of peroxide. This is again a consequence of the gradual incorporation of the larger molecules to the gel fraction and the continuous generation of low molecular weight species as a result of scission reactions. Similar results were observed in the chromatograms obtained from the irradiated and peroxi treated samples of the *EG8400* copolymer.

DSC characterization

The low crystallinity character of the original samples has been already discussed. The crystallization and melting properties of cross-linked samples either by β-irradiation or DCP were examined. Table II shows the thermal properties (T_m, ΔH_m, T_c, and ΔH_c) of peroxide cross-linked and β-irradiated copolymers. In the case of peroxide cross-linked samples, despite its low degree of crystallinity and the low size of their crystals, there is a continuous decrease in the melting and crystallization temperatures and enthalpies with increasing DCP concentrations. In this case, the cross-linking reactions take place in the melt, and therefore, the new cross-links generated in this process induce additional restrictions to crystallization, reducing the length of the crystallizable chains. Within the range of DCP concentrations employed in this study, an almost linear decay of the crystallization enthalpies with the amount of peroxide was observed for both polymers.

The data from Table II reveal also a very slight decrease in the melting and crystallization temperatures of the irradiated copolymers. At low irradiation doses, the changes are not significant. Only at the higher radiation dose a tenuous drop in those properties is perceived. The observed differences in behavior with respect to the peroxide cross-linked copolymers may be explained by the fact that the irradiation of the original polymers took place at room temperature. Consequently, it is expected that the new cross-links will be formed preferentially in the amorphous regions without affecting the crystallizable portions of the chains. Even though, a slight temperature rise may be expected to occur on the samples as a consequence of the irradiation process depending on the specific heat of the material and the irradiation dose. In this work, to avoid significant temperature rises in the samples, the desired doses were applied in several steps (as explained in the Experimental Section), so that the heat can be dissipated to the surroundings of the sample. Irrespective of this precaution, due to the wide range of the melting temperatures displayed by these copolymers, some of the more imperfect crystals may have been affected by the irradiation procedure, especially when the higher doses were applied.

Rheological characterization

The rheological properties in shear of β-irradiated ethylene-1-octene copolymers have been obtained under small-amplitude oscillatory experiments at several temperatures between 30°C and 90°C, at 10°C intervals, but only the results at the lowest and the highest temperature are displayed here. Figure 4(c,d) shows the evolution of the elastic modulus, G′, for both copolymers at 90°C when increasing doses of radiation are applied. At this temperature, where the crystalline structures of the original polymers are completely molten, the rheological behavior is dominated by the chemical links generated by radiation. The values of G′ measured for the modified *EG8411* copolymers on the terminal zone at equivalent doses are consistently higher than those corresponding to *EG8400* and evolve towards a higher plateau modulus. This reflects again the influence of the higher concentration of short chains present in the *EG8400* and the higher efficiency achieved by the radiation cross-linking on *EG8411*. At low radiation doses, an immediate shift of the terminal zone toward lower frequencies is observed but no significant changes appear in the transition to the rubbery plateau. The polymers irradiated with 100 kGy are very close to the critical dose for incipient gelation. At this point, the G′ and G" curves straighten over the entire frequency range and the loss tangent, Tan δ, becomes frequency independent [see Fig. 4(e,f)]. Beyond 100 kGy, the G′ curves at low frequencies move towards a low frequency plateau, which eventually should converge to the equilibrium modulus.

The rheological behavior at 30°C is dominated by the weak crystalline structure of the polymers. Figure 4(a,b) shows the evolution of G′ versus frequency of the two copolymers after been treated with increasing doses of β radiation. The elastic modulus of the original *EG8411* copolymer is considerably higher than that of *EG8400* over the entire range of the frequency window explored. This reflects the greater crystalline content of the copolymer with lower octene concentration. At this temperature, a slight irradiation with 25–50 kGy does not introduce any significant change in the viscoelastic behavior of any of the two modified copolymers. At 100 kGy and beyond, a progressive decay in the magnitude of the elastic modulus is clearly observed over the entire frequency range covered by the experiments. This is attributable to the decrease of the crystalline content induced by radiation at the higher doses that was reported and discussed in the section referred to the thermal behavior of these polymers and also to scission reactions.

The results from the cross-linking induced by DCP at 90°C are reported in Figure 5(c–f). When *EG8411* was processed with 0.5% DCP, an incipient post-gel condition was achieved. Concentrations of DCP above 0.5% resulted in well cross-linked gels with sol fractions ranging from 0.50 to 0.98. These cross-linked copolymers exhibit very low and invariant Tan δ values over the entire frequency window diminishing progressively with increasing concentrations of the peroxi modifier. The viscoelastic behavior of the DCP modified *EG8400* was similar to that of *EG4811*.

For the higher DCP concentration (4%), G′ was also almost constant on the whole range of frequencies for both copolymers. In this case, G′ ≅ 0.12 MPa at 90°C. This value was lower than those obtained at high frequencies with concentrations of peroxide of 1 and 2%. The reason for this decay of the elastic modulus with increasing amounts of peroxi modifier may be attributed to chain scission reactions that are common in these copolymers with considerably concentration of tertiary carbons and were confirmed by the SEC chromatograms performed on the soluble fractions of the post-gel peroxi modified polymers.

At 30°C, the viscoelastic behavior is again dominated by the crystalline morphology. Both copolymers exhibit slightly increasing G′ values with frequency in the original and on the peroxi modified materials. The magnitudes of the elastic modulus versus frequency curves tend to diminish with

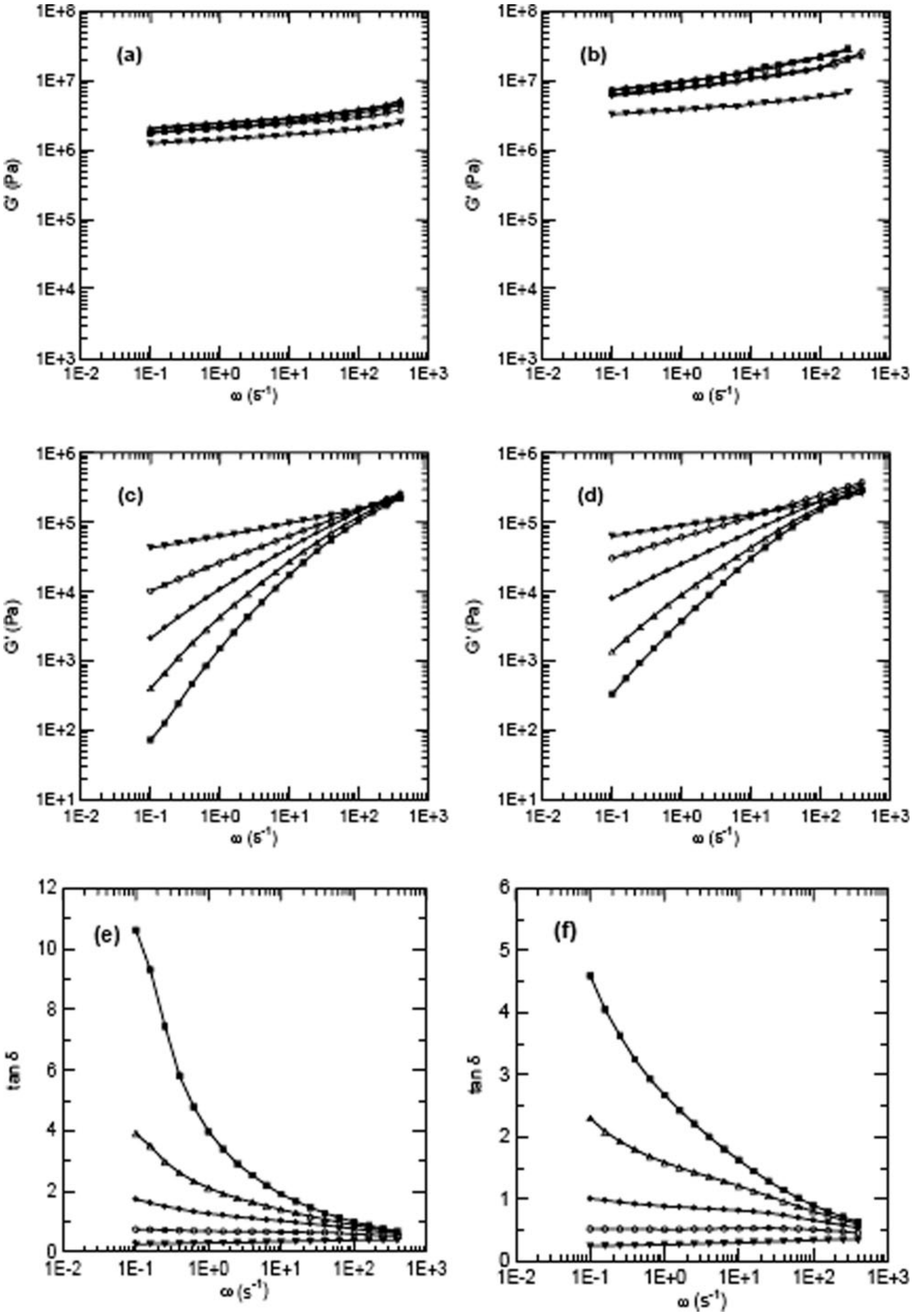

Figure 4 Rheological properties versus frequency for β-irradiated copolymers: Storage modulus (G′) at 30°C for (a) *EG8400*, (b) *EG8411*; Storage modulus (G′) at 90°C for (c) *EG8400*, (d) *EG8411*; Loss Factor (Tan δ) at 90°C for (e) *EG8400*, (f) *EG8411*. (■) neat polymer, (Δ) 25 kGy, (●) 50 kGy, (○) 100 kGy, and (▼) 200 kGy.

increasing peroxide concentration due to the interference caused by the cross-links on the length of the chains able to enter in the crystalline phase.

FTIR characterization

The degradation process related to carbonyl oxidation was monitored by FTIR analysis for the β-irradiated and DCP cross-linked samples. The contribution of carbonyl groups (aldehydes, ketones, and acids) was evaluated integrating the area of the peaks in the range between 1705 and 1750/cm. The reference band corresponding to $(CH_2)_n^-$ $(n \geq 4)$ rocking at 721/cm, which is not affected during the corresponding cross-linking process was used as an internal standard.[32]

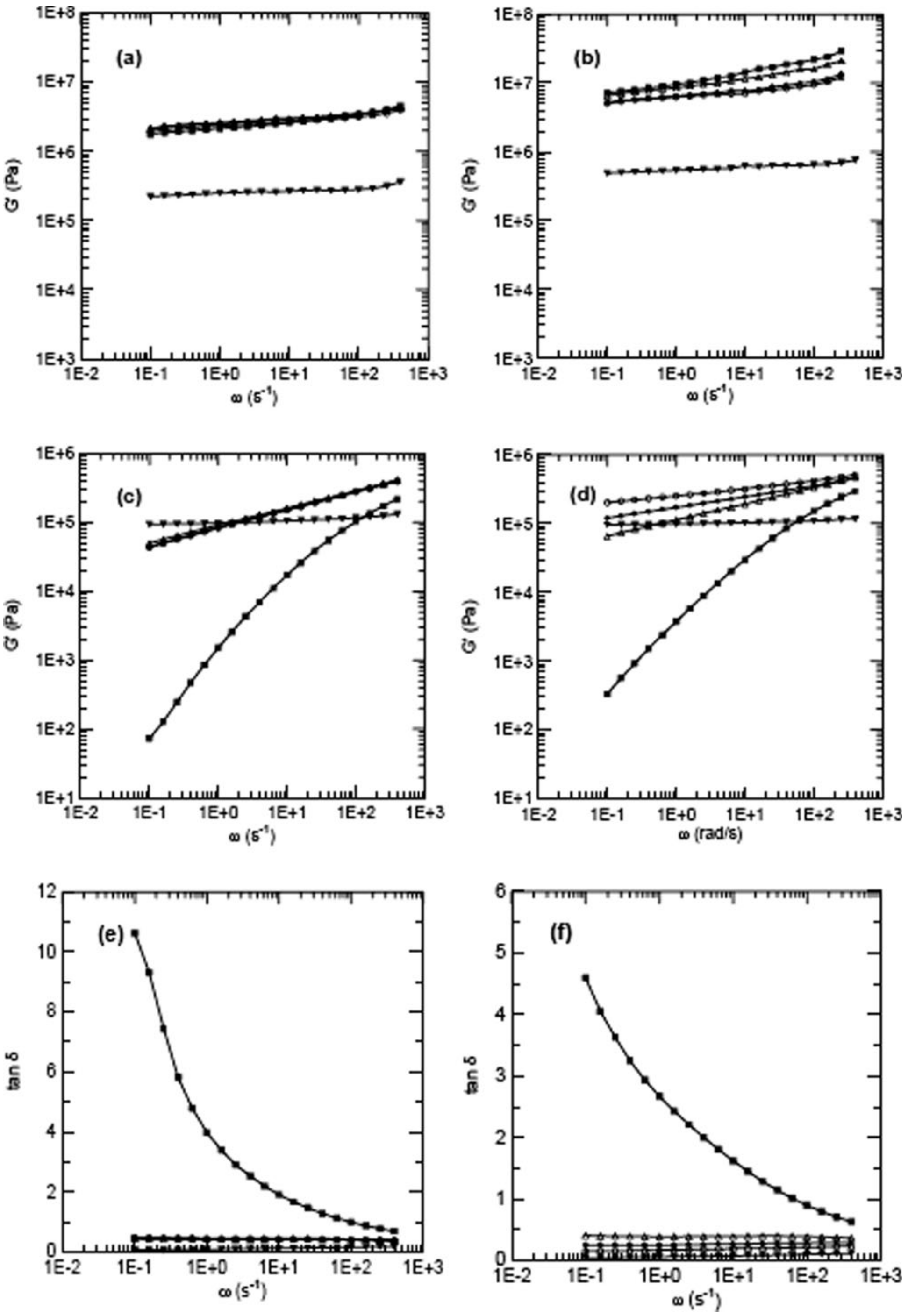

Figure 5 Rheological properties versus frequency for DCP modified copolymers. Storage modulus (G′) at 30°C for (a) *EG8400*, (b) *EG8411*; Storage modulus (G′) at 90°C for (c) *EG8400*, (d) *EG8411*; Loss Factor (Tan δ) at 90°C for (e) *EG8400*, (f) *EG8411*. (■) neat polymer, (Δ) 0.5% DCP, (●) 1% DCP, (○) 2% DCP, and (▼) 4% DCP.

Practically no differences were detected in the region of the spectra corresponding to the carbonyl region between the original polymers and the irradiated materials. There is in accordance with previous results obtained with electron beam irradiation on a ethylene-octene copolymer (Affinity *EG8200*) were no obvious signs of oxidation were found with radiation doses up to 500 kGy.[30] In contrast, peroxide modified samples showed a growth of the magnitude of this region at the higher concentrations of DCP.

Gel content

Irradiation of both copolymers gave a post-gel condition only in the case of the higher irradiation dose

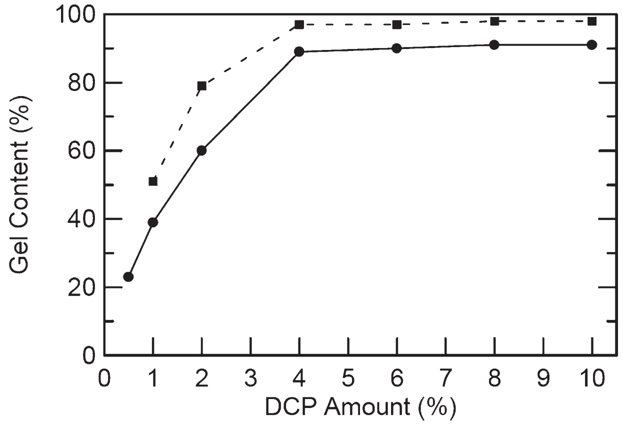

Figure 6 Gel content of DCP cross-linked ethylene-1-octene copolymers. (●) *EG8400* and (■) *EG8411*.

of 200 kGy. With this condition a gel content of 68% was obtained for *EG8411* and 58% for *EG8400*. This difference is attributed to the higher comonomer content in *EG8400*, which makes it more prone to chain scission as was previously explained.

To explore the maximum amount of soluble fraction obtainable on these copolymers with DCP, additional experiments were performed on both copolymers with doses of DCP up to 10% peroxide. The values of the gel content obtained with increasing doses of DCP are displayed in Figure 6. In this case, the gel content obtained with similar concentrations of DCP on both copolymers results in a higher gel content for *EG8411* on the whole range of peroxide concentrations explored. While peroxi modification of the *EG8411* with concentrations of 4% or higher resulted in a fully cross-linked polymer with negligible soluble content (less 2%). On the other hand, *EG8400* with higher octene concentration gave soluble fractions not lower than 9%. Apparently, according to these results, the tertiary carbon content has a high incidence on the final gel content that can be obtained by the DCP cross-linking process.

Mechanical properties

Table III shows the tensile properties of peroxide and β-radiation cross-linked ethylene-1-octene copolymers. The stress–strain curves in all cases present no localized yield and a continuous rise of the elongational force was observed. This is attributable to the low size of the crystalline structure of the polymers and the complex branched structure of the modified polymers. The tensile strength of the β-irradiated cross-linked samples increases progressively, reaching its maximum value at 200 kGy. Moreover, the biggest increase in the tensile strength takes place between 100 kGy and 200 kGy.

On the other hand, the elongation at break also increases progressively up to 100 kGy, where the failure occurred at a deformation higher than 1100%, and then dropped slightly at 200 kGy. The increase in the elongation at break is related to the growth in the molecular weight and the complexity of the molecular chains. These results are in good accordance with the changes in molecular weight observed up to 100 kGy through the SEC characterization. At high irradiation doses (200 kGy), the post-gel condition is obtained. This result is in agreement with the enhancement of the tensile strength and a reduction of the elongation at break.

The values of tensile strength obtained in the peroxide cross-linked copolymers are lower than those of the irradiated samples. The maximum value for the tensile strength corresponds to a DCP amount of 1% for *EG8400* and between 1 and 2 phr for *EG8411*. Beyond these doses, a progressive decay of the tensile strength and elongation and break is observed for both copolymers. This is in accordance with the decay observed on the elastic modulus versus frequency measurements showed in the rheological measurements. A comparison can be made between the copolymers *EG8400* modified with 200 kGy and that treated with 2 phr DCP since both have very similar gel fractions (60%). In this condition, higher tensile strength and elongation at break was

TABLE III
Tensile Properties of Cross-Linked Copolymers

		Tensile strength (MPa)		Elongation at break (%)	
		EG8400	*EG8411*	*EG8400*	*EG8411*
Irradiation dose (kGy)	0	2.88 ± 0.11	5.75 ± 0.07	956 ± 63	916 ± 24
	25	3.39 ± 0.01	7.86 ± 0.89	1076 ± 52	1022 ± 51
	50	3.20 ± 0.07	7.97 ± 0.28	1135 ± 54	1040 ± 8
	100	5.09 ± 0.86	9.33 ± 0.57	1389 ± 167	1106 ± 51
	200	11.39 ± 0.83	14.80 ± 2.08	1372 ± 69	1054 ± 97
DCP amount (phr)	0.5	7.80 ± 0.81	9.74 ± 2.18	1383 ± 83	878 ± 172
	1	7.94 ± 1.17	12.40 ± 0.29	1387 ± 163	927 ± 27
	2	4.78 ± 0.98	13.12 ± 0.05	931 ± 147	434 ± 3
	4	2.56 ± 0.44	6.23 ± 0.65	166 ± 82	390 ± 30

obtained on the irradiated copolymer. This may be a consequence of the different distribution of cross-linked points obtained with the irradiation procedure at room temperature with respect to that performed in the molten state when DCP is utilized and to the quality of the crystalline structure of both materials.

CONCLUSIONS

Metallocene ethylene-1-octene copolymers with narrow molecular weight distribution and a high comonomer content exhibit very low crystallinity and a very wide melting range that almost overlaps with the glass transition. In the DSC characterization of cross-linked samples, peroxide cross-linking in the molten state allows the introduction of scission and cross-linking reactions at any site of the copolymer chains reducing the length of repeated units available for crystallization. Therefore, enthalpies and melting and crystallization temperatures decrease. Crystal size in both copolymers is low, so the changes induced in crystalline morphology are not considerable. On the other hand, as irradiation takes place at room temperature, samples modified by this procedure exhibit only slight changes in crystallinity. FTIR spectroscopy has been used to determine that a higher degree of oxidation after cross-linking results when peroxide modification is employed.

It has been verified that the comonomer content, which is related to the amount tertiary carbons and to the degree of cristallinity of the ethylene-octene copolymers reduces the efficiency of the cross-linking process. In particular, the higher amount of tertiary carbons and lower crystallinity in *EG8400* diminishes the cross-linking efficiency with respect to *EG8411* when irradiation is applied. With DCP modification in the molten state, where crystallinity does not play any role, the lower content of terciary carbons in *EG8411* makes the modification procedure more efficient than with *EG8400*, especially at high DCP doses.

The SEC technique combined with the rheological characterization provided very useful tools to study the evolution of molecular structure with the progress of cross-linking and chain scission.

The cross-linking process improves significantly the tensile properties of both copolymers. Within the range of doses explored in this work, β-radiation provided better tensile properties than DCP cross-linked copolymers. On the peroxide modified samples, optimal mechanical properties were obtained with concentrations of about 1% DCP.

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