



Effect of DBPH and vacuum gamma radiation on metallocenic ethylene-1-hexene and ethylene-1-octadecene copolymers

A.J. Satti^{a,c,*}, N.A. Andreucetti^a, R. Quijada^b, C. Sarmoria^c, E.M. Vallés^c

^a Laboratorio de Radioisótopos, Dpto. de Química, Universidad Nacional del Sur (UNS), 8000 Bahía Blanca, Argentina

^b Departamento de Ingeniería Química, Fac. Ciencias Físicas y Matemáticas, Universidad de Chile, 2777 Santiago, Chile

^c Planta Piloto de Ingeniería Química, PLAPIQUI, (UNS-CONICET), Camino "La Carrindanga", Km 7, CC 717-8000 Bahía Blanca, Argentina

ARTICLE INFO

Article history:

Received 17 July 2009

Accepted 7 August 2009

Keywords:

Polyethylene copolymers

Gamma irradiation

Mathematical model

Metallocene catalyst

ABSTRACT

Two different post reactor processes were compared, ⁶⁰Co vacuum gamma irradiation and chemical modification with 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane (DBPH), on two metallocenic copolymers. These copolymers have a similar molecular weight and crystallinity, but different side chain lengths and concentration of end vinyl groups. The influence of the crosslinking agents on the structure of the samples was studied using gel extraction, size exclusion chromatography (SEC), FTIR spectroscopy and differential scanning calorimetry (DSC). The analysis of the data indicates that crosslinking reactions predominated over scission reactions in all cases. At the same conversion, peroxide modified samples show higher crosslinking levels than irradiated samples. The modified polymers show a complex rheological behavior and an increment in their rheological properties due to crosslinking. FTIR data demonstrated a depletion of vinyl terminal groups with the increment of the absorbed dose and the peroxide concentrations applied. This depletion was more significant in the peroxide crosslinked samples. A mathematical model that accounts for scission and crosslinking reactions fitted well the experimental data.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

The modification of polyethylene by means of post reactor processes is used to obtain new materials with specific final properties. The most common post reactor processes are the treatment with ionizing radiations (Andreucetti et al., 1999; Charlesby, 1960; Dole, 1972; Li et al., 2002; Machi, 1995; Perraud et al., 2003; Satti 2009; Vallés et al., 1990) and the chemical modification with agents like the organic peroxides (Gloor et al., 1994; Kwei et al., 1991; Pérez et al., 2002). Both treatments induce the generation of free radicals, which in turn produce chemical reactions that result in the crosslinking and scission of the polymer chains. Crosslinking prevails in polyethylene, increasing the viscoelastic properties and improving the resistance to high temperatures and solvents in the modified polymer.

The objective of this work is to compare and analyze the two processes of modification on two different copolymers of the polyethylene family obtained by copolymerization of ethylene with 1-hexene and 1-octadecene. Metallocene synthesis made possible the homogeneous distribution of the comonomer along the main

chain in both copolymers. In this way, an analysis of the modifying reactions on the structure of these copolymers allows the evaluation of the influence of the modification procedure on the concentration of isolated tertiary carbons along the polymer chains and on the different length of the short branches inserted during the copolymerization reaction. In order to achieve the main objective of the present paper, a broad range of doses of radiation and peroxide concentrations was studied. To the best of our knowledge, it is the first time that these many variables are used for the study of both modification processes on ethylene copolymers with similar percentage incorporation of 1-hexene and 1-octadecene.

The changes on the polymers structure were followed by gel extraction, size exclusion chromatography (SEC) combined with multi-angle laser light scattering (MALLS), Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and rheology. Also, a mathematical model that accounts for scission and crosslinking reactions was implemented and used to fit the experimental data.

2. Experimental

2.1. Polymerization

The polymers shown in Table 1 were synthesized using a 11 Parr reactor with stirring (500rpm) at 60 ° with an ethylene

* Corresponding author at: Laboratorio de Radioisótopos, Dpto. de Química, Universidad Nacional del Sur (UNS), 8000 Bahía Blanca, Argentina. Tel.: +54 0291 4861700 281; fax: +54 0291 4861600.

E-mail addresses: asatti@plapiqui.edu.ar (A.J. Satti), andreuce@criba.edu.ar (N.A. Andreucetti), raquijad@ing.uchile.cl (R. Quijada), csarmoria@plapiqui.edu.ar (C. Sarmoria), valles@plapiqui.edu.ar (E.M. Vallés).

pressure of 2 bar. The catalyst/co-catalyst used for this synthesis was $\text{Et}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$, and the solvent was toluene. (Escudero et al., 2008). The amount of comonomer incorporated in the copolymers was measured by ^{13}C NMR at 80°C using a VARIAN XL-300 spectrometer operating at 75 MHz (Villar et al., 2001). Table 1 shows the obtained results. The nomenclature used to identify the copolymers is of the type PEX# where X and # are the letter and number that identify, respectively, the comonomer used (H = 1-hexene, OD = 1-octadecene), and the amount of comonomer incorporated.

2.2. Irradiation procedure

The copolymers were compression molded to 1-mm-thick flat sheets using a hydraulic press at 180°C for 2 min and a maximum pressure of 10 MPa. Then, the sheets were allowed to cool at room temperature outside the press and placed inside Pyrex tubes, attached to a vacuum glass line, and left under high vacuum for 24 h. The samples were then sealed in those same tubes. Irradiation of the samples was performed at room temperature with a ^{60}Co γ -source. The absorbed doses ranged from 7 to 103 kGy. They were measured with a Red Perspex dosimeter. Following irradiation, the polymer samples were annealed for 2 h at 140°C to assure undetectable levels of long-living radicals (Rijke and Mandelkern, 1971).

2.3. Modification with organic peroxides

2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane (DBPH) was used as the peroxide initiator of the modification process. Fractions of fine powders of the synthesized copolymers were impregnated with different amounts of peroxide-hexane 0.5% w/v solution to give the desired final peroxide concentrations once the solvent was removed. The quantities of peroxide added to each copolymer ranged from 800 to 15,700 ppm. The impregnated polyethylenes were placed between 3-mm-thick steel plates held apart by a 0.5-mm-thick brass frame. The samples were then compression molded between the hot plates of a hydraulic press for 15 min at 170°C and 10 bar. Then the pressure was relieved and the samples were kept at 170°C between the plates for 15 min. The reaction time and temperature were chosen on the basis of previously done rheological experiments (Bremner and Rudin, 1993; Pérez et al., 2002).

No significant oxidative degradation was observed in either of the two processes of modification.

2.4. Characterization

Sol-gel analysis: After annealing the irradiated polymers, the Pyrex glass tubes were cut open. Sol-gel analysis was performed to measure the insoluble gel fraction. For this purpose, samples were weighed, packed in paper filters, placed inside round bottom flasks, immersed in an oil bath at 130°C and extracted five times with fresh xylene for 24 h. About 0.5 wt% Irganox 1010 was added and nitrogen was bubbled continuously during extraction to avoid oxidation of the samples. After the extraction cycle was completed, the samples were precipitated, washed with cold methanol and vacuum dried to a constant weight.

Size exclusion chromatography: The molecular weight of the materials was determined by SEC in a Waters 150C ALC/GPC with three PLgel Mixed-A $300 \times 7.5 \text{ mm } 20 \mu\text{m}$ columns (Polymer Laboratories) and two detectors: refractive index (RI) (Waters) and a multi-angle laser light scattering (MALLS) (Dawn DSP, Wyatt Technology Corporation). The solvent used was 1,2,4-trichlorobenzene, at 135°C and 1.0 ml/min. The columns were calibrated with narrow molar mass distribution standards of polystyrene (Pressure Chemical) and polyethylene (NIST).

Fourier transform infrared spectroscopy: The concentration of the different unsaturations present in the original and irradiated polymers was determined using a Nicolet 520 FTIR Spectrometer. For this purpose, films were prepared by melt pressing the materials at 150°C using a hydraulic press. The spectra were recorded at a 4 cm^{-1} resolution over the range of $4000\text{--}400 \text{ cm}^{-1}$ with air as background. Quantitative data on the vinyl groups and trans-double bonds in the samples before and after radiation treatment were calculated from the FTIR spectrum (Chum, 1992; Dole, 1979).

Differential scanning calorimetry: The thermal transitions were determined using a Perkin-Elmer Pyris 1 calorimeter under argon atmosphere and calibrated with indium and *n*-heptane standards. In order to ensure the same thermal history for all samples, the original and irradiated copolymers were first heated from 25 to 150°C ($10^\circ\text{C}/\text{min}$), maintained at 150°C for 2 min, and then cooled down from 150 to -40°C at $10^\circ\text{C}/\text{min}$. After this treatment, the samples were heated again at the same heating rate and the corresponding endotherm was recorded between -40 and 150°C . The melting peaks and the corresponding areas were determined to give both the melting temperature (T_m) and enthalpy of fusion (ΔH_f). To estimate the degree of crystallinity of the polymers, we used a ΔH_f value of 288 J/g for the melting enthalpy for 100% crystalline PE (Mirabella and Bafna, 2002).

Rheology: The rheological characterization of the molten polymers was carried out in nitrogen atmosphere using a Rheometrics RDA-II rheometer with 25 mm parallel plate geometry. The viscoelastic properties of the polymers (elastic modulus G' and viscous modulus G'') were measured in small-amplitude

Table 1
Properties of the ethylene/1-hexene and ethylene/1-octadecene copolymers synthesized for this work.

Name	% molar comonomer incorporation ^a	M_w (kDa) ^b	M_n (kDa) ^c	PD ^c	γ irradiation		DBPH		Terminal vinyl content ($\times 10^4 C = C/1000 C$) ^d	Trans unsaturation content ($\times 10^4 C = C/1000 C$) ^d
					D_{gel} (kGy) Exp.	D_{gel} (kGy) Model	D_{gel} (ppm) Exp.	D_{gel} (ppm) Model		
PEH9	9.2	86.4	29.7	2.1	36	38	2610	2250	224	96.0
PEOD7	7.1	89.5	48.6	1.76	36	33	2730	2370	520	47.3

Obtained by.

^a ^{13}C -NMR.

^b SEC-MALLS.

^c SEC-RI.

^d FTIR.

oscillatory shear flow as a function of frequency and temperature. Frequencies used ranged between 0.04 and 400 s⁻¹ and temperatures between 80 and 180 °C according to the melting point of the polymers. To ensure the linear relation between stress and deformation, small strains were used in all the dynamic tests, which were selected from previously performed strain sweeps.

2.5. Mathematical model

A mathematical model was used to analyze the experimental data of the modified material. It is a mean-field model based on probability theory. It considers both crosslinking and scission (Andreucci et al., 1998; Sarmoria and Vallés, 2004). It is assumed that all bonds are equally likely to react, that there are no substitution effects and no intramolecular reactions. The input parameters for this model are the molecular weight and molecular weight distribution (MWD) of the virgin polymer, the relative proportion of crosslinking and scission reactions, and a measure of the gel point. Depending on the particular treatment studied, that measure is the irradiation dose or the peroxide concentration at the gel point. The model calculates pregel molecular weights, postgel molecular weights of the soluble fraction, plus the sol and gel fractions.

3. Results and discussion

3.1. FTIR characterization

FTIR spectroscopy was used in order to follow the evolution of double bonds for both copolymers, as the modifying procedures were applied. The usual unsaturations present in these metallo-cenic copolymers are the terminal vinyl groups (908 cm⁻¹: P-CH=CH₂), the trans-vinylenes (966 cm⁻¹: _lCH=CH^l) and the vinylidene groups (894 cm⁻¹: >C=CH₂) (Quijada et al., 1995).

The decay of the vinyl unsaturations with the different doses of radiation or peroxide was compared for both copolymers. In order to facilitate the comparison between the two modification procedures the critical point to reach the gel in both copolymers, D_{gel} , either by irradiation or chemical modification, was used as the normalization parameter. The extent of reaction produced on the polymers was calculated as D/D_{gel} , where D corresponds to either absorbed dose or peroxide concentration. Fig. 1 shows that the decrease of the terminal vinyl-group content with increasing D/D_{gel} is more pronounced in PEOD7 than in PEH9, regardless of the treatment used. This may be at least partially attributed to the greater initial content of vinyl groups in PEOD7, compared with that of PEH9 (Table 1) (Smedberg et al., 1997).

Comparing both types of modification, it is evident that the crosslinking process with DBPH consumes the vinyl terminal groups more rapidly. The chemical modification in the molten state is characterized by the higher mobility of the macroradicals and the vinyl terminal groups. This together with the very important difference in temperature between the chemical and the irradiation procedure accounts for the dissimilar rates of consumption of the vinyl groups in both processes.

Trans-double bonds only changed significantly for the irradiated samples, as may be seen in Fig. 2. For both copolymers a linear increase of the concentration of trans unsaturations was observed with the dose. This is attributed to the dehydrogenation of two nearby main chain carbons with the successive liberation of gaseous hydrogen molecules from the polymers (Dole, 1979; Lyons and Johnson, 1993; Mandelkern, 1972; Perraud et al., 2003). FTIR analysis also showed that the concentration of vinylidene double bonds (894 cm⁻¹), originally produced during the

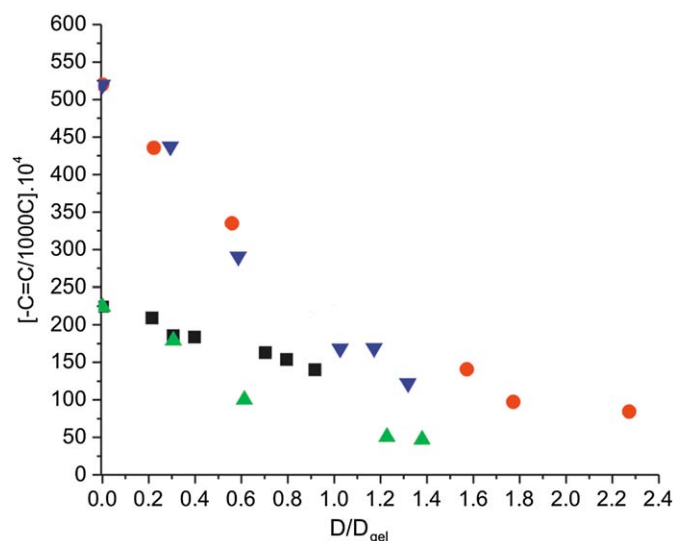


Fig. 1. Decrease of terminal vinyl double bonds with the increase of D/D_{gel} , for: ■, irradiated PEH9. ●, irradiated PEOD7. ▲, DBPH modified PEH9. ▼, DBPH modified PEOD7.

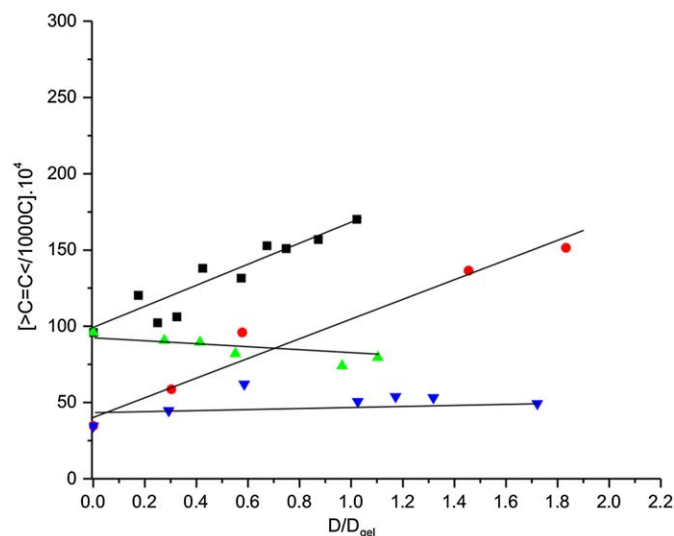


Fig. 2. Increase of trans-vinylene double bonds with D/D_{gel} for: ■, irradiated PEH9. ●, irradiated PEOD7. ▲, DBPH-modified PEH9. ▼, DBPH modified PEOD7.

metallic polymerization of the copolymers, was not significantly affected by any of the modifying treatments.

3.2. Sol-gel analysis

The polyethylene chains reticulate as a result of the crosslinking reactions. When conversion reaches D_{gel} , an insoluble and infusible network appears. Its value depends on the molecular characteristics of the chains, and on the efficiency of the modification processes. This critical parameter was calculated plotting the measured gel fractions versus the absorbed radiation or peroxide dose and extrapolating the gel fraction to zero gel. The values obtained for each copolymer are reported in Table 1. Please note that similar experimental D_{gel} values were obtained for both copolymers either by irradiation or peroxide modification. This suggests that the length of the short chain branches incorporated to the polyethylene chains by the copolymerization with hexene and octadecene has no major influence on the efficiency of each modification process.

The evolution of the gel fraction with conversion is also expressed here in normalized form as w_{gel} vs. D/D_{gel} . The results, shown in Fig. 3a, exhibit a continuous increase in gel fraction with the intensity of the modification procedures. The evolution of the gel fractions for both treatments tend to coincide in the vicinity of the gel point and far past the gel point, but are different at intermediate normalized conversions. In this transitional region the peroxide treatment produces more gel than the irradiation treatment. This may be attributed to the fact that peroxide treatment is done in the melt, since radicals on the molten samples have higher diffusion possibilities than in the solid state.

3.3. Gel point and gel fraction

We used the model described in Section 2.5 to fit the increase of gel fraction as the modification progresses. Instead of using the experimentally measured gel points, we estimated them through an optimization that employed Marquardt's method to minimize the objective function (Marquardt, 1963),

$$F = \sum_{i=1}^{N_{\text{exp}}} (w_{\text{gel},i}^{\text{exp}} - w_{\text{gel},i}^{\text{mod}})^2 \quad (1)$$

where the superscripts "exp" and "mod" refer to experimental or modeled values, respectively. The critical gel doses obtained in this way are also reported in Table 1 and compared with those found by extrapolation to zero of the experimental gel fraction. The agreement is good, with differences below 15% in all cases.

After finding the optimal gel points it was possible to simulate the evolution of the sol fraction with dose or peroxide concentration. We show in Fig. 3a the resulting fitting curves. The different lines ensuing from the model predictions shown in the figure correspond to the different polydispersities of the original samples. A good theoretical fit for all samples may be observed. Since the model ignores the presence of side chains altogether, this result is consistent with the observation that the length of the side chains appeared to have no significant effect on the experimentally found gel points.

3.4. SEC-RI-MALLS characterization

The evolution of the molecular weight changes due to scission and crosslinking reactions brought up by the induced macroradicals was determined by SEC with a double detection (RI and MALLS) system. By coupling SEC with MALLS, the absolute molar

mass of every fraction can be determined directly. Fig. 3b shows the experimental measurements of the pregel and postgel M_w values, obtained by MALLS for the samples of the gamma and DBPH modified copolymers. With the gel point values found from fitting the gel fractions in Fig. 3a, simulations were performed to predict the weight average molecular weights. The results from the model are also shown with continuous lines in Fig. 3b. Here the measured values for M_w of the different modification procedures have also been normalized by dividing each weight average molecular weight determined by MALLS by M_{w0} , the weight average molecular weights of the original copolymers. The theoretical curves for the samples with different polydispersities overlap closely in the pregel region and may not be distinguished. We may observe that the prediction is very good for all samples in both irradiation and peroxide treatments.

The normalized chromatograms obtained with the RI detector of the original and modified PEH9 copolymers in the pregel region are presented as an example in Fig. 4. In this case we have chosen to show the chromatograms obtained with the RI detector because they are more sensitive to detect the lower molecular weight species. This allows monitoring more closely the evolution of scission reactions in the low molecular weight tail of the chromatogram. In the case of the irradiated polymers, a significant rise of the concentration of high molecular weight species with increasing dose is observed on the high molecular weight side of the normalized peaks (Fig. 4a). This is a consequence of the crosslinking reactions induced by macroradical recombination. On the contrary, the changes in concentration visualized on the low molecular weight species on the left side of the graph are almost negligible.

Fig. 4b shows the equivalent results for the peroxide modified polymers. An important feature in this case is that a displacement of the entire chromatogram towards higher M_w values results as the concentration of peroxide increases. This displacement is not observed on the irradiated samples. The diversity in behavior between the two modification procedures may be attributed to the differences in reactivity between the two treatments. The chemical modification is distinguished by the higher mobility of the macroradicals and vinyl terminal groups in the molten state. In principle, the formed peroxide radicals have equal probability of attacking each of the hydrogen atoms that belong to the copolymer chains to form very reactive macroradicals. This gives the heavier molecules of the molecular weight distribution a higher probability of reaction. If vinyl terminal groups are available for reaction with the formed macroradicals on the ends

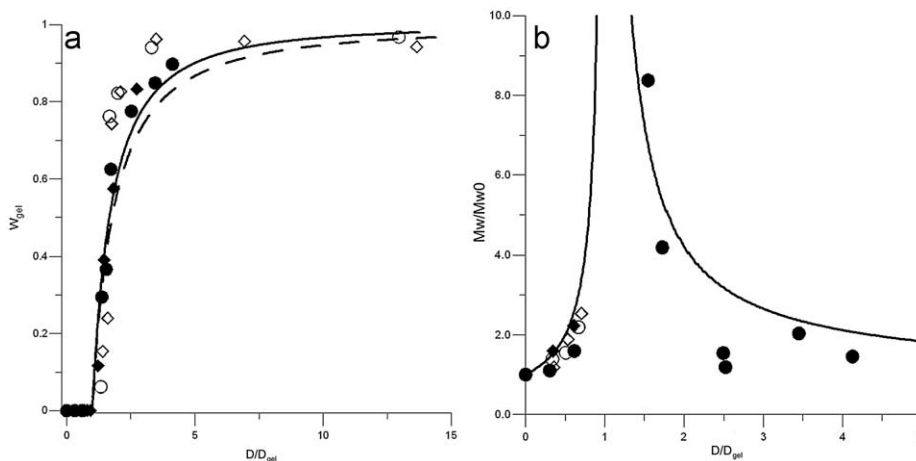


Fig. 3. (a) Gel fraction vs. D/D_{gel} and (b) normalized weight average molecular weight, M_w/M_{w0} , vs. D/D_{gel} , for \blacklozenge irradiated PEH9, \bullet irradiated PEOD7, \diamond DBPH modified PEH9, \circ DBPH modified PEOD7. Dashed lines represent the theoretical predictions for PEH9, while solid curves represent the theoretical predictions for PEOD7.

of the polymer molecules of the whole distribution, every molecule possessing a vinyl end would have the same probability of reaction irrespective of its length. The addition of the vinyl terminated chains to the available macroradicals should give as a result the formation of branched structures of higher molecular weight at the expense of the species emanating from the whole distribution producing a result consistent with the shift observed on the SEC chromatograms (Aigbodion et al., 2009; Satti, 2009). This observation is also consistent with the more rapid consumption of the vinyl terminal groups reported in the FTIR section for the peroxide modified copolymers.

3.5. Rheology

The viscoelastic properties of the original copolymers and the changes induced by increasing doses of absorbed radiation and organic peroxide in PEH9 were studied making use of sinusoidal dynamic oscillation experiments at different temperatures.

The evolution of the elastic (G') and loss (G'') modulus with frequency at different irradiation and peroxide doses for the PEH9 copolymer at 140 °C are shown in Fig. 5. An increment in both G' and G'' in the terminal zone was observed for the pregel modified samples near $D/D_{gel} \approx 1/3$ (13 kGy or 800 ppm), but only mild changes appear in the transition to the rubbery plateau. This is a clear indication that the formation of long-chain branches is the

main structural change induced by these modification processes. Long-chain branching affects long-time relaxations, but does not modify notably the local behavior of short segments of the polymer chains that are the ones that dominate the viscoelastic performance at high frequencies. Also slightly longer relaxation times are observed for the peroxide modified samples at equivalent doses as revealed by the higher G' values measured on the terminal region. The rheological behavior of the peroxide modified samples confirms the higher level of crosslinking attained with this procedure as was observed by the SEC technique.

A shift of the cross-over modulus, G_{co} (defined as the point where $G' = G''$), toward lower frequencies is also observed. At a D/D_{gel} near 1/3, the cross-over modulus occurs at lower frequencies than in the case of the original copolymers. The shift of G_{co} for the peroxide modification is greater than for irradiation. This is another indication of the greater rheological complexity due to the more extensive chain branching and reticulation obtained in the modification with organic peroxides.

Closely after the gel point, $D/D_{gel} \approx 1.2$ at 42 kGy or 3200 ppm depending on the modification procedure, the slopes of G' and G'' remained similar for the entire frequency range analyzed, with G' higher than G'' . This kind of behavior is typical of the incipient gelation and entirely similar to some of our previous results on irradiated model polyethylene–butene copolymers obtained by hydrogenation of anionically polymerized butadiene (Vallés et al.,

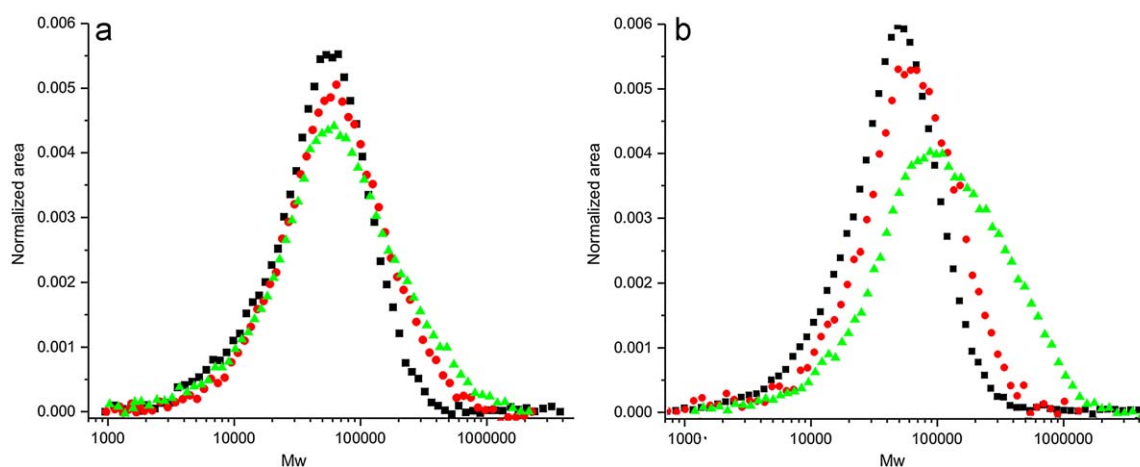


Fig. 4. SEC-RI chromatograms of virgin PEH9 and a) irradiated samples and b) DBPH modified samples, at different D/D_{gel} : ■, virgin PEH9. ●, $D/D_{gel} = 1/3$. ▲, $D/D_{gel} = 0.6$.

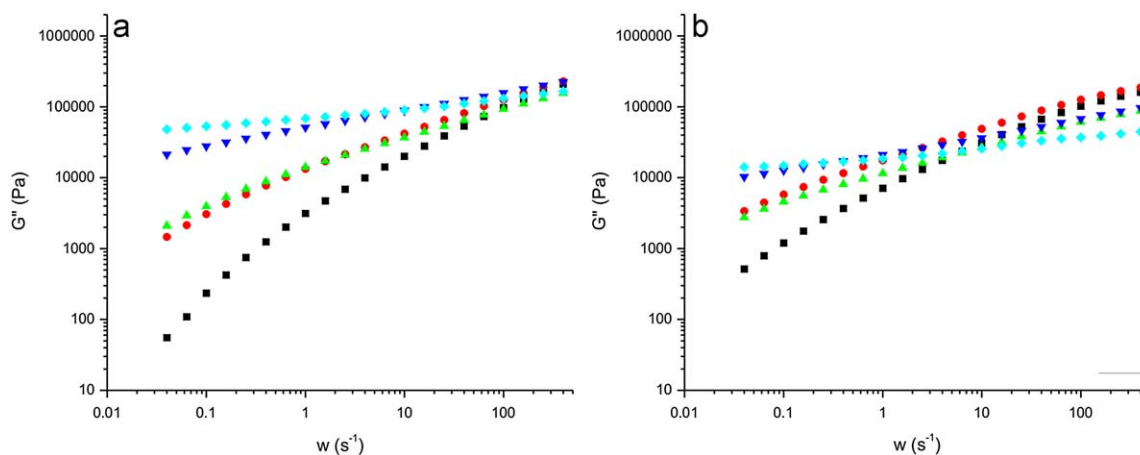


Fig. 5. Linear viscoelastic behavior at 140 °C for the (a) G' and (b) G'' moduli, for modified samples of PEH9: ■, unmodified sample. ●, irradiated at $D/D_{gel} = 1/3$. ▲, DBPH modified at $D/D_{gel} = 1/3$. ▼, irradiated at $D/D_{gel} = 1.2$. ◆, DBPH modified at $D/D_{gel} = 1.2$.

1990) and other PEH irradiated copolymers (Satti, 2009; Satti et al., 2009). The larger separation between G' and G'' curves and their lower slopes for the sample modified with peroxides, also indicates a higher crosslinking level.

Further details for the rheological behavior of this copolymer can be found elsewhere (Satti, 2009; Satti et al., 2009).

3.6. DSC Characterization

The DSC technique was also used in order to analyze the morphology changes with the modifying processes. The original crystallinities of the samples (28% for PEH9 and 31% for PEOD7) were not significantly affected with either of the two modification procedures. Only a small shift to lower values of the melting point (T_m) was observed for all the modified samples, as reported in Table 2. This depletion is a consequence of the increasing number of crosslinks induced by the modification methods, which are excluded from crystallites, inhibiting to some extent the crystal growth process and inducing the formation of more crystalline defects.

4. Conclusions

In this work we explored the effect of two different modification processes, gamma irradiation and chemical modification with DBPH in the melt, on two different ethylene copolymers synthesized with an Et[Ind]₂ZrCl₂/MAO metallocene catalyst. The polymers were synthesized to be similar in all respects but the length of the side chains.

The effects of the crosslinking and scission reactions induced by these procedures on the molecular structure of the different copolymers were evaluated by SEC and extraction techniques. It was observed that these treatments lead to the crosslinking of the original copolymers, with a negligible level of scission reactions. These results indicate that, within the range of comonomer incorporation of short side chains covered by this work, scission does not seem to be affected significantly by the increment in main chain tertiary carbons introduced by the copolymerization with hexene and octadecene. The different length of short chain

branches has no influence, either. Moreover, the evolution of the amount of gel was fitted well with a theoretical model that does not take into account the presence of the short chain branches in the original copolymers.

A decrease in the concentration of the terminal vinyl groups with increasing absorbed dose or peroxide concentration was observed in the FTIR spectra for the two copolymers. This decay was more pronounced for the PEOD copolymer, under the two modification techniques studied in this work. FTIR characterization also showed a similar increase of the trans unsaturated groups for both irradiated copolymers, although no significant changes were observed on the concentration of these groups for the modification of the copolymers with organic peroxides.

After analyzing data obtained from SEC, gel extraction and rheology, it was concluded that the chemical attack with peroxides constitutes a more efficient way of producing crosslinking than irradiation, at least in the range of dose studied. Furthermore, the decrease of terminal vinyl groups observed by FTIR was more significant in the treatment with DBPH. As these groups are mainly consumed in crosslinking reactions, this would provide a plausible explanation for the main differences observed in the two modification procedures. As the peroxide modification is performed in the melt, where there are fewer restraints to the mobility of the macroradicals and vinyl terminal groups, higher crosslink content is expected when the polymers are compared at equivalent modification levels with respect to the gel doses. In view of these results it seems interesting to compare the peroxide modification process with that of irradiation in the melt at an equivalent temperature. Unfortunately we do not have access to an irradiation facility that can operate at high temperatures.

Acknowledgements

The authors wish to thank Universidad Nacional del Sur and CONICET (Argentina), Universidad de Chile, Universidad de Valladolid (Spain) and specially Project CYTED VIII. 11 for supporting this work.

References

- Aigbodion, A.I., Ressia, J.A., Giolino, A.E., Failla, M.D., Vallés, E.M., 2009. The effect of vinyl concentration on the structural and rheological characteristics of peroxide modified high-density polyethylenes. *J. Appl. Polym. Sci.*, in press.
- Andreucetti, N.A., Sarmoria, C., Curzio, O., Vallés, E.M., 1998. Effect of the phenolic antioxidants on the structure of gamma-irradiated model polyethylene. *Radiat. Phys. Chem.* 52, 177–182.
- Andreucetti, N.A., Fernández Lagos, L., Curzio, O., Sarmoria, C., Vallés, E.M., 1999. Model linear ethylene–butene copolymers irradiated with gamma-rays. *Polymer* 40, 3443–3450.
- Bremner, T., Rudin, A., 1993. Peroxide modification of linear low-density polyethylene: A comparison of dialkyl peroxides. *J. Appl. Polym. Sci.* 49, 785–798.
- Charlesby, A., 1960. *Atomic Radiation and Polymers*. Pergamon Press, London.
- Chum, S.P., 1992. Effects of vinyl chain-ends on the melt viscoelastic properties of radiation crosslinked polyethylene. *J. Plast. Film Sheet.* 8, 37–47.
- Dole, M., 1972. *The Radiation Chemistry of Macromolecules*, Vol. I–II. Academic Press, New York.
- Dole, M., 1979. Cross-linking and crystallinity in irradiated polyethylene. *Polym. Plast. Technol. Eng.* 13, 41–64.
- Escudero, M.A., Quijada, R., Vallete, M.C., 2008. Thermal oxidation of metallocene ethylene-1-olefin copolymer films during one year oven aging. *Polym. Degrad. Stab.* 93 (10), 1947–1951.
- Gloor, P.E., Tang, Y., Kostanska, A.E., Hamielec, A.E., 1994. Chemical modification of polyolefins by free radical mechanisms: a modelling and experimental study of simultaneous random scission, branching and crosslinking. *Polymer* 35, 1012–1030.
- Kwei, T., Pearce, E., Schlecht, M., Cheung, W., 1991. Crosslinking and scission in radical-promoted functionalization of polyethylene. *J. Appl. Polym. Sci.* 42, 1939–1941.
- Li, J., Peng, J., Qiao, J., Jin, D., Wei, G., 2002. Effect of irradiation on ethylene–octene copolymers. *Radiat. Phys. Chem.* 63, 501–504.

Table 2

Melt points for the original and modified samples, corresponding to (a) the gamma irradiation in vacuum and (b) the modification with DBPH.

Name	Dose (kGy)	T_m (°C)
(a)		
PEH9	0	82.11
PEH9 20	23	76.16
PEH9 40	41	76.15
PEH9 70	69	74.62
PEH9 100	103	73.97
PEOD7	0	84.26
PEOD7 20	20	80.544
PEOD7 50	51	78.35
PEOD7 120	113	78.36
(b)		
Name	Concentration (ppm)	T_m (°C)
PEH9	0	82.11
PEH9p 16	1583	76.34
PEH9p 32	3167	76.34
PEH9p 79	7917	74.15
PEOD7	0	84.26
PEOD7p 16	1583	80.53
PEOD7p 32	3167	80.53
PEOD7p 79	7917	78.34

- Lyons, B.J., Johnson, W.C., 1993. Radiolytic formation and decay of trans-vinylene unsaturation in polyethylene. In: Reichmains, E., Frank, C.W., O'Donnell, J.H. (Eds.), *Irradiation of Polymeric Materials: Processes, Mechanisms and applications*, Vol. 527. American Chemical Society, Washington, D.C., pp. 62–73.
- Machi, S., 1995. Radiation technology for sustainable development. *Radiat. Phys. Chem.* 45, 399–410.
- Mandelkern, L., 1972. XIII: radiation chemistry of linear polyethylene. In: Dole, M. (Ed.), *The Radiation Chemistry of Macromolecules*, Vol. I. Academic Press, New York, pp. 321.
- Marquardt, D.W., 1963. An algorithm for least squares estimation of nonlinear parameters. *J. Soc. Ind. Appl. Math.* 11 (2), 431–441.
- Mirabella, F.M., Bafna, A., 2002. Determination of the crystallinity of polyethylene/ α -olefin copolymers by thermal analysis: relationship of the heat of fusion of 100% polyethylene crystal and the density. *J. Polym. Sci., Part B: Polym. Phys.* 40, 1637–1643.
- Pérez, C.J., Cassano, G.A., Vallés, E.M., Failla, M.D., Quinzani, L.M., 2002. Rheological study of linear high density polyethylenes modified with organic peroxide. *Polymer* 43, 2711–2720.
- Perraud, S., Vallat, M., Kuczynski, J., 2003. Radiation crosslinking of poly(ethylene-co-octene) with electron beam radiation. *Macromol. Mater. Eng.* 288, 117–123.
- Rijke, A.M., Mandelkern, L., 1971. Irradiation of linear polyethylene Partitioning between sol and gel. *Macromolecules* 4, 594–599.
- Quijada, R., Dupont, J., Lacerda Miranda, M.S., Scipioni, R.B., Galland, G.B., 1995. Copolymerization of ethylene with 1-hexene and 1-octene: correlation between type of catalyst and comonomer incorporated. *Macromol. Chem. Phys.* 196 (12), 3991–4000.
- Sarmoria, C., Vallés, E., 2004. Model for a scission-crosslinking process with both H and Y crosslinks. *Polymer* 45, 5661–5669.
- Satti, A.J., 2009. Doctoral Thesis. Department of Chemistry, Universidad Nacional del Sur, Argentina.
- Satti, A.J., Andreucetti, N.A., Quijada, R., Sarmoria, C., Pastor, J.M., Vallés, E.M., 2009. γ -Irradiated Metallocenic Polyethylene And Ethylene–1-Hexene Copolymers. Unpublished results.
- Smedberg, A., Hjertberg, T., Gustafsson, B., 1997. Crosslinking reactions in an unsaturated low density polyethylene. *Polymer* 38, 4127–4138.
- Vallés, E.M., Carella, J.M., Winter, H.H., Baumgaertel, M., 1990. Gelation of radiation crosslinked polyethylene. *Rheol. Acta* 29, 535–542.
- Villar, M.A., Failla, M.D., Quijada, R., Maler, R.S., Vallés, E.M., Galland, G.B., Quinzani, L.M., 2001. Rheological characterization of molten ethylene– α -olefin copolymers synthesized with Et[Ind]₂ZrCl₂/MAO catalyst. *Polymer* 42, 9269–9279.