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Modification of Model Ethylene-Butene Copolymers Using Gamma Radiation and an Organic Peroxide

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Summary: Well-characterized linear ethylene-butene copolymers with polydispersities lower than 1.1 were modified using gamma radiation and an organic peroxide with the purpose of assessing the relative importance and form of evolution of the chain-linking processes with these two methods. The copolymers used in this work were obtained by hydrogenation of polybutadienes, which were synthesized by anionic polymerization of butadiene. Part of these materials were irradiated by gamma rays in a ^{60}Co radiation facility and the rest was modified with 2,5-dimethyl-2,5 di(terbutyl peroxy)-hexane in the molten state. As expected, the critical radiation dose and the critical concentration of peroxide required for the onset of gelation decreases with average molecular weight of the original copolymer. Although, the chain-linking reactions govern the modification process, there is a fraction of molecular chains that suffers scission. The measurable fraction of molecules having molecular weights lower than the original quasi-monodisperse copolymers is, for both processes, about 5% of the total modified polymer. On the post-gel region, the gel amount increases continuously with the radiation dose and the peroxide concentration added to the copolymers. For the radiation modified polymers, the calculation of the evolution of the molecular weights assuming ideal network forming conditions agreed very well with the experiments both, before and after the gel point. This is not accomplished when the modification process is done with the use of peroxides. Also, the results obtained from the peroxide modification processes at low relative concentrations with respect to the critical one for gelation show that the evolution of the structural modification evolves at a considerable lower rate than that observed in the radiation results.

Keywords: crosslinking; ethylene-butene copolymers; irradiation; organic peroxide

1. Introduction

Polyethylene (PE) is widely used because it combines low cost with properties that bring adaptability to a great variety of applications. In an effort to improve the physical and mechanical properties of this polymer and extend its range of use, many processes have been developed. Crosslinking is among the most broadly post-reactor modification procedures applied to PE. The aim of the process is to modify the molecular structure of the material in such way as to improve its thermo-mechanical stability and, also, wear and chemical resistance. There are various alternative methods for introducing crosslinks between the polyethylene chains, but ionizing radiation and organic peroxide crosslinking are among the most commonly used in the industry.[1,2] Both of these methods are based on generating free macroradicals that follow mainly combination reactions originating linkages between the chains of the polymer. This induces an increment in

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branching and molecular weight or, if higher doses of radiation or peroxides are employed, the formation of a three-dimensional network.[1–4]

The radiation and peroxide crosslinking procedures differ from each other in the chemical nature of the process, even though it is considered that the product obtained by either method has similar characteristics. One of the main advantages of irradiation crosslinking is that it can be applied to the already shaped solid material and the principles governing the absorption of high-energy ionizing radiation are well established.[3,4] For most high-energy radiations of practical interest the bulk of the energy is eventually deposited in the medium through the release of fast electrons, which can generate excited molecules conducting to free radicals by scission of covalent bonds.[1–4]

The modification of polyethylene using organic peroxides is usually carried out in the molten state. The advantage of this method over radiation is that it may be carried out with the normal equipment commonly used for the processing of polyolefins. At the processing temperatures of the polymer, the homolytic scission of the peroxide O–O bonds generates oxy-radicals. Then, the oxy-radicals extracted hydrogen atoms from the saturated chains producing macroradicals, which may follow various chemical reactions that alter the molecular structure of the polymer. The main reaction in the process is the combination of macroradicals to generate cross-links.[1]

It is well known that when polyethylene undergoes mainly chain linking, the molar mass increases with the intensity of the applied modification process, until it reaches infinitely large values. If the degree of crosslinking increases even further, a molecular network or gel starts forming. This phenomenon is called gelation and marks the transition from the liquid state to the solid state. Previous to the gel point, all the molecules are finite in size, able to flow, and can be dissolved in appropriate solvents. After gelation, an infinite molecule (the gel) is formed and it is insoluble and unable to flow. At this stage, the gel grows with either the radiation dose or peroxide concentration becoming a large fraction of the total mass.[1–4]

The chain linking reactions are convenient for improving the polyethylene properties. Nevertheless, there are other competitive reactions that take place during the radiation or chemical crosslinking processes affecting its efficiency and the molecular structure and final properties of the modified polymer.[1–13] The competition between chain-linking and secondary reactions determines the evolution of the molecular weight, the critical concentration required to form the first gel and the course of the partitioning between gel and soluble fractions. For each one of the modification processes, a combination of various factors has been found to determine the relative importance of those reactions. Among the most important are the molecular structure of the original PE, that is the average molecular weight, the molecular weight distribution and the presence of tertiary carbons and vinyl groups.[1–19,21] Nevertheless, there are other factors to be taken into account because they also affect the modification process, for instance, the irradiation dose and the semicrystalline structure of PE when irradiation is applied at relatively low temperature,[1–4,9,10] type and concentration of peroxide,[1,14,15,21] and external factors as well, such as the environment and the temperature.[1–4,14,15]

Although the effect of either high energy ionizing irradiation or peroxide crosslinking on polyethylene has been extensively studied, the influence of the factors cited above on the relative importance of the main reactions that take place in the modification of PE is not completely understood. There are studies reaching comparable or contradictory results. For example, there are authors concluding that chain-linking is the main reaction that occurs during the modification. While, others have suggested that reaction such as chain-scission and creation of carbon double bonds can also play an important role in the process. It has also been suggested that chain scission is likely to occur in a larger extension in branched polyethylene than in high-density linear polyethylene.[1,3,4,16]

The difficulties are, at least in part, due to the fact that most of the studies have been carried out using commercial polymers. These polymers usually have very broad molecular weight distribution and chains with different structures that produce rather heterogeneous materials. The lack of a good characterization of the molecular structure of the initial polymers, together with its complexity, has obscured the analysis and interpretation of the experimental results. Studies dealing with model polymers of homogeneous chemical structure can be an alternative route in trying to establish the competition of the reactions that take place during the modification process. In an effort directed to solve some of these questions, there have been studies in the past dealing with fractions of linear PE, substances consisting in low molecular weight analogues to polyethylene, and other model polymers.[4–6,17–19]

In this paper, we present some of the latest results found in our work on irradiation and peroxide crosslinking of hydrogenated polybutadienes (HPB). These polymers, which can be considered ethylene–butene random copolymers, were obtained from the catalytic hydrogenation of monodisperse linear polybutadienes produced by anionic polymerization. The use of this model material with homogeneous chemical structure, a controlled number of short branches and very narrow weight distribution simplifies the quantitative analysis and allows sorting out the complexity introduced by the chemical heterogeneity typical of commercial polymers. The HPB were irradiated by gamma rays in a ^{60}Co radiation facility using an ample range of doses. The peroxide crosslinking of the HPB was carried out in the molten state using various concentrations of 2,5-dimethyl-2,5-di(terbutylperoxy)-hexane. The techniques of Size Exclusion Chromatography (SEC) combined with Light Scattering (LS) and selective extraction with solvent were used to characterize the molecular structure of the original and modified polymers. The evolution of molecular weight of the soluble and the gel fraction with the radiation dose and concentration of the peroxide was established. In addition, the molecular weight dependence of the critical concentration required for incipient gel formation was determined. Also, the dynamic mechanical properties of the molten state were evaluated for some of the modified HPB.

2. Experimental

2.1. Materials

The linear polybutadienes (PB) were synthesized by anionic polymerization of butadiene under high purity conditions following standard methods.[20] The polymerization was carried out in cyclohexane solution, under high vacuum and at room temperature. Tertiary buthyl-lithium was used to initiate the reaction, and isopropanol was the termination reagent. Infrared spectroscopy (IR) was used to determine the double-bond microstructure of the polybutadienes. The IR spectra of the samples, which were reordered using a Nicolet 520FT-IR spectrometer, revealed that about 7% of the butadiene molecules were added to the growing chain of all the PB following a 1,2-addition path.

The resulting polybutadienes were subsequently hydrogenated in solution of toluene using either a heterogeneous Palladium or homogeneous Wilkinson's (RhCl $(PPh_3)_3$) catalyst. The hydrogenation was performed at 90 °C in a Parr reactor, working at 5 MPa of hydrogen pressure. Residual unsaturation was monitored from absorption peaks at 910 cm^{-1} and 966 cm^{-1}. The analysis of the IR spectra of the hydrogenated polymers gave no evidence of any absorption bands that can be associated to double bonds. The hydrogenated polybutadienes (HPB) have a molecular structure chemically similar to random ethylene-butene copolymers with a composition of about 20 CH_3/1000 C.

Size Exclusion Chromatography (SEC) was used for the determination of the molecular weights and molecular weight distribution of the HPB. Table 1 reports the materials employed in this study and their average molecular weights. The polymers are named HPB#, where # is the number that identifies the weight average molecular weight of the polymer. The SEC runs were made at 135 °C using 1,2,4 trichlorobenzene (TCB) as solvent on a Waters 150-C ALP/GPC having a set of five PLGel columns from Polymer Labs with nominal porous sizes of 10^6, 10^5, 10^4, 10^3 and 500 A. The SEC equipment was equipped with a refractive index (RI) detector and with an on-line Multi Angle Light Scattering detector (LS) from Wyatt Technology (Dawn DSP). The average molecular weights, Mn-LS and Mw-LS, were estimated using the commercial program named ASTRA developed by Wyatt Technology Corp. Also, the number average molecular weights of the HPB polymers employed in gamma radiation modification were measured by membrane osmometry (MO) and reported in Table 1. The osmometer used was a Knauer model 01.00 and the solvent was TCB at 90 °C.

2.2.1. Modification Using ^{60}Co Gamma Radiation

The irradiation of HPB-50 and HBP-100 polymers was performed using a ^{60}Co gamma source. All the samples were irradiated in vacuum at 25 °C and some of them also at 135 °C. The samples for room temperature irradiation were compression molded at 120 °C under vacuum. After this, they were sealed under vacuum in Pyrex tubes and irradiated with a ^{60}Co source at Centro Atómico Ezeiza. The irradiation doses applied ranged from 5 kGy to 160 kGy. After irradiation at room temperature, the polymer samples were annealed for 2 hours at 140 °C to allow free radicals decay. The irradiation doses were measured with a Red Perspex dosimeter. A small amount of samples of HPB-100 polymer were vacuum gamma irradiated at high temperature at Tokio University. Sample preparation was similar to that for vacuum irradiation at room temperature. The dosage ranged from 30 kGy to 100 kGy.

2.2.2. Modification Using an Organic Peroxide

The 2,5-dimethyl-2,5-di(terbutyl peroxy)-hexane (DBPH) used as initiator of the chemical modification process, was kindly supplied by Akzo Chemical of Argentina. The HPB copolymers in the form of fine powder were impregnated with different amounts of a peroxide-hexane solution. The hexane was allowed to evaporate over a period of 16 hs under hood to obtain the desired final concentrations of peroxide in the polymer. This method provides a homogeneous dispersion of the peroxide on the polymer.[14,21] The concentration of peroxide ranged from 0.05 to 4 wt%.

The impregnated HPB's were placed between 3 mm thick steel plates lined with

Table 1.
Average molecular weights of the HPB polymers.

Polymers for Chemical Modification			
Polymer	Mn-LS (g/mol)	Mw-LS (g/mol)	Cc (wt%)
HPB-29	27,000	29,000	0.7%
HPB-45	44,000	45,000	0.5%
HPB-81	80,000	81,000	0.2%
HPB-114	113,000	114,000	0.12%
HPB-125	123,000	125,000	0.1%
Polymers for Radiation Modification			
Polymer	Mn-MO (g/mol)	Mw-LS (g/mol)	Dgel
HPB-50	45,000	50,000	75 kGy
HPB-100	102,000	108,000	34 kGy

aluminum foils and held apart by a 1mm thick brass frame. The samples were then compression molded between the hot plates of a hydraulic press for 30 min at 170 °C. Initially a low pressure was applied to mold the polymer, which was then released. A polymer free of peroxide was tested under those conditions in order to verify if degradation due to ambient oxygen was present. No sign of alteration of the molecular structure was observed.

The reaction time necessary to assure complete reaction was estimated by performing rheological tests following the method used by Bremner et al. for monitoring curing reactions.[21] They consisted in performing a peroxide modification of the HPB between the plates of a rheometer operating in the dynamic mode. The elastic dynamic modulus (G') was continuously measured at 170 °C at a frequency of 10 s^{-1} using samples previously press molded for 5 min at 130 °C. The period of time elapsed until G' of the reacting sample reached a constant value was considered to be the total reaction time. It was found to be approximately seven times larger than the halftime of the peroxide, which is approximately 4 min at 170 °C according to the technical information given by the supplier.

2.3 Molecular Characterization

The gel fraction was determined by extracting the soluble portion of the different specimens of each chemical and radiation modified polymer. The samples were extracted in soxhlet extractors with xylene at 135 °C to obtain the polymer soluble fractions. Nitrogen was bubbled continuously to avoid oxidation of the samples and also a small amount of Irganox 1010 was added as antioxidant. The total time of extraction varied between 36 and 72 h depending on the sample.

The percentage of gel reported in this work is an average of those obtained from three or four specimens of each one of the modified polymers. The manipulation of the samples necessary for carrying out the extraction of soluble and the small mass weighted contributes to some dispersion in the data value. The molecular weight and molecular weight distribution of the soluble fractions of the different modified polymers were determined by SEC. The tests were performed under similar conditions to those used for characterizing the HPB. No correction for chain branching was applied.

2.4 Rheological Characterization

The dynamic elastic, $G'(\omega)$, and viscous, $G''(\omega)$, moduli of all materials were measured using small-amplitude oscillatory shear flow experiments using a rotational rheometer from Rheometrics Inc. (model RDA-II). The dynamic–mechanical experiments were run using parallel plates, 25 mm in diameter, frequencies ranging from 0.01 to 500 s^{-1} and temperatures between 140 °C and 200 °C. All the tests were performed using small strains to ensure the linearity of the dynamic responses. Also, nitrogen atmosphere was used to prevent oxidation of the samples during sample preparation and during the tests.

3. Results and Discussion

HPB modifications were studied using seven hydrogenated polybutadienes with polydispersities lower than 1.1. Their average molecular weights, which are presented in Table 1, ranged from 29,000 to 125,000 g/mol. The modification of these polymers with the DBPH peroxide was studied on five of the original polymers using concentrations of peroxide ranging from 0.02 to 4 wt%. Gamma radioinduced modification was studied on two polymers with a chemical structure entirely similar to those used previously in the peroxi-modification process, and also with similar molecular weight.

The range of peroxide concentration and radiation doses employed in this study allowed to establish the critical concentration for gelation and to determine the evolution of the gel with increasing peroxide and radiation doses for all the HPB's. Since the polymers used were practically monodisperse, SEC elution curves were very sensitive to changes in the molecular weight induced by the radiation treatment and by chemical modification. Below the gel point, significant changes in the molecular weight distribution of the original polymers were observed. Figure 1 shows as an example the normalized SEC curves of the polymers obtained from the modification of HPB-50 with increasing radiation doses below the gel point, which was attained in this case at 75 kGy. The traces of the original narrow distribution HPB polymer are also included as a reference in the figure. At the high molecular weight side it can be observed the formation of a population of molecules having molar masses significantly larger than the original one. These new species are a consequence of the combination of macroradical reactions that generate intermolecular linkages. The proportion of such molecules raises as the gamma radiation doses increases becoming an important fraction of the total mass of the polymer.

On the low molecular side of the distribution in Figure 1, new molecules are present with molar masses lower than the original. They result from chain-scission processes. The amount of the scissioned species is significantly lower than that resulting from crosslinking reactions, but they are clearly distinguished in the inset that amplifies the low molecular weight region. The SEC-LS outcome is accurate enough to clearly confirm that there is a competition between chain-linking and chain scission for this particular system. Qualitatively, similar changes in the molar mass distribution were observed for all the polymers obtained from the radiation and chemical modification. We have estimated that the mass fraction of scissioned material amounts to 4% of the modified polymer in HPB-50. Similar results, (less of 6% of scissioned material), were observed for the rest of the HPB polymers both vacuum irradiated at 25 °C and at 135 °C and chemically modified with DBPH.

The evolution of the high molecular weight tails that result from the chemical modification with increasing amounts of peroxide have a similar behavior than those obtained by gamma irradiation, but a minor proportion of the high molecular weight molecules is observed in this case when the date are compared at equivalent doses relative to that corresponding to the critical

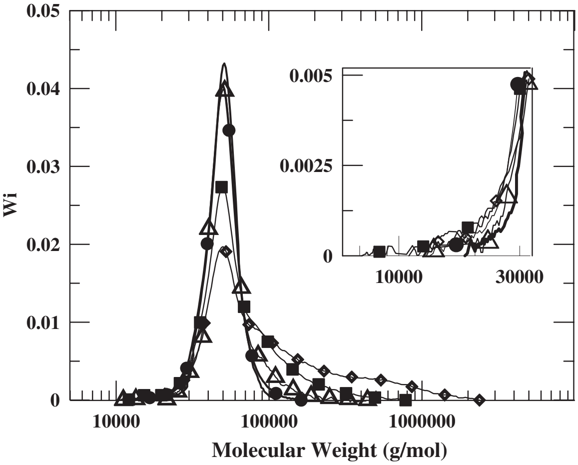
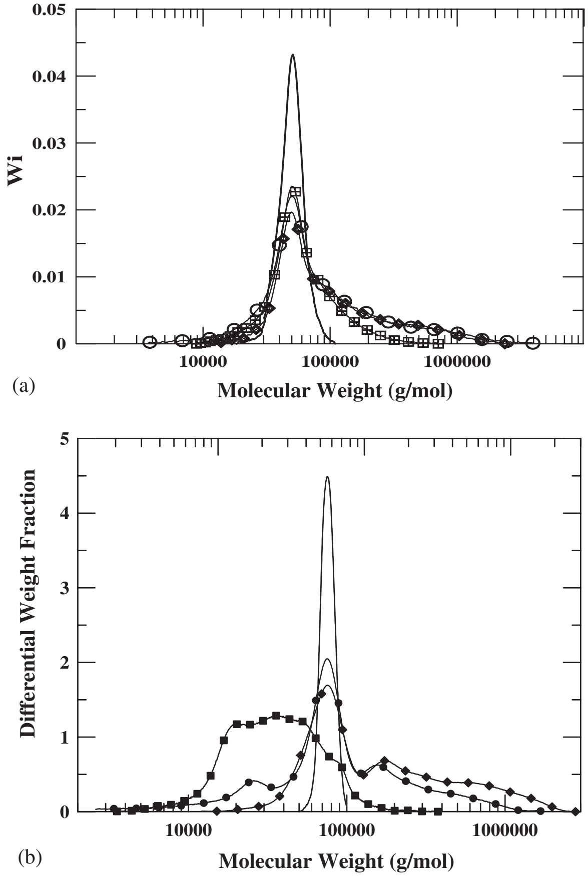


Figure 1.
SEC traces of the original and radiation modified HPB-50 polymer irradiated at room temperature. The chromatograms were normalized to have the same area. The radiation doses are below the critical gelation dose, *Dgel* = 75 kGy. ***Reference:*** (▬) original polymer; (●) 10 kGy, (△) 20 kGy; (■) 40 kGy; (%) 75 kGy.

gel dose. Column 4 in Table 1 reports the critical gel radiation doses and peroxide concentrations for all the HPB's.

After the gel point, only the soluble fraction of the modified material can be studied by SEC. Figure 2 a) presents the molecular distribution of the soluble part corresponding to the HPB-50 polymer modified by vacuum gamma radiation at room temoerature and Fig. 2 b) shows the molecular weight distribution of some of the soluble postgel fractions for the HPB-81 polymer modified by peroxide. The traces of the narrow molecular weight distribution of the original HPB polymers were also included in these figures for reference.

Since the gel grows at the expense of the sol by preferentially incorporating the largest molecules, the soluble fraction is enriched in low molecular weight material while depletion of the larger molecular weight species with increasing doses or radiation or peroxide concentration is observed. In the cases of the HPB-81 modified with concentrations of peroxide of 3 wt%, the distribution is mainly formed by molecules with molar mass lower than the original. At this level of modification of



(a)

(b)

Figure 2.

a) SEC traces of the original and radiation modified HPB-50 polymer at room temperature, normalized to have the same area. The radiation doses are above of the critical gelation dose, *Dgel* = 75kGy. ***Reference***: (▬) original polymer; (%) 75 kGy; (○) 80 kGy and (I) 119 kGy. b) SEC traces of the original and chemically modified HPB-81 polymer normalized to have the same area. The peroxide concentrations are above of the critical gelation concentration, Cc = 0.2wt%. ***Reference***: (▬)original polymer; (◆) 0.3 wt%,(●) 1 wt%; (■) 3 wt%.

the HPB-81 the soluble part is just 5% of the specimen mass.

It seems helpful to compare the postgel SEC chromatogram for 0.3 wt% peroxide concentration (which corresponds to a concentration 50% greater than critical gel concentration Cc = 0,2 wt% for HPB-81) in Figure 2b) with the SEC traces for 119 kGy postgel dose (58% greater than Dgel = 75 kGy) in Figure 2a). At these particular reaction conditions, we assume that both processes are comparable because they have employed approximately a 50% more peroxide concentration or radiation dose respect to the value required to reach the gel point. As a result of this comparison, it can be seen that the right hand side of the SEC traces diminishes more rapidly in the radiation process. This implies that the evolution of crosslinking reactions at equivalent doses with respect to the critical dose for gelation is more rapid in the case of radiation than in the modification with peroxide.

The evolution of the amount of gel, (expressed as percentage of the total mass) as a function of the relative gel dose is presented in Figure 3 a) for all the irradiated polymers. This was obtained dividing the radiation dose applied in each case, by the critical gel dose found for each polymer by extrapolating the experimental measured gel fractions to zero gel concentration. Beyond the gel point the amount of gel increases rapidly with radiation dose reaching values larger than 90%. The experimental data have been compared with the theoretical model proposed in reference [5] where we have modeled the irradiation process under ideal network formation conditions.

The model assumes that i) the irradiation process is random; that is, all monomer units are equally likely to be subject to scission, ii) all reactions are independent, iii) there are no intramolecular reactions and iv) the ratio of crosslinking to scission is taken to be constant during the entire irradiation process. This model is an extension of the model proposed by Miller and Macosko for the polymerization of chains with length and site distribution.[22,23] The model was extended to evaluate the evolution of the weight and number average molecular weights of the HPB samples over the entire range of radiation dose (pre and postgel zone) and the progress of the gel fraction with the dose of radiation applied to the original polymers. A ratio of 5% scission was employed in the calculations, this value was an average of the scission levels that were estimated from the SEC traces. The bars in each data point represent the scattering in the experimental values that was observed. An excellent reproduction of the evolution of the experimental results with the dose of radiation was found.

Figure 3b) shows the equivalent results to those reported in Figure 3a) for the progress in the gel fraction with increasing amounts of peroxides. Qualitatively, a similar trend to that observed in the radiation modified polymers was observed. All the gel fraction data obtained after modifying the HPB with the peroxide describe the same trend. Moreover, they seem to delineate the same curve. This suggests that the peroxi-modification induces similar evolution of the gel amount for all the polymers regardless of their initial molecular weight. If the molecular weight would had a noticeable effect on the peroxide efficiency, a distinctly trend in the evolution of the gel fraction should have been observed among the polymers. It can be noticed that the amount of gel developed in the materials depends on the initial molecular weight of the polymer. For a given concentration of peroxide, lower amounts of gel were obtained as the molecular weight of the original polymer diminished.

The solid line in Figure 3 b) represents the theoretical curve of the evolution of the gel fraction with respect to the relative concentration of DBPH. The same amount of scission (5%) than that used in the modeling of the radiation results was employed in the calculations. The results from the peroxide crosslinking reveal that there is a considerable deviation of the

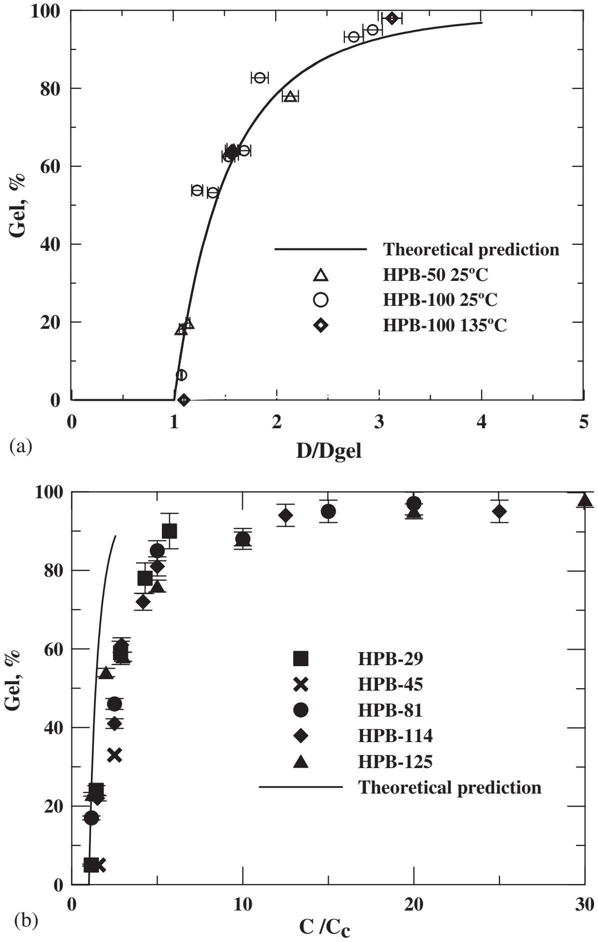


Figure 3.
a) Proportion of gel (expressed as percentage) of the radiation modified HPB polymers as a function of the normalized radiation dose (D/Dgel). b) Proportion of gel (expressed as percentage) of the chemically modified HPB polymers as a function of the normalized peroxide concentration (C/Cc).

experimental data from the theoretical expectation. The deviation is in such a direction that much less gel is produced than the one predictable. Nevertheless, for values of C/C_c greater than 15 the gel produced seems to reach asymptotically values very close to 100%. One plausible reason for this is that the either oxy or alkyl radicals may be consumed in secondary reactions producing inert species, which reduce the efficiency of the process.

The evolution of the theoretical and experimental weight average molecular weights for HPB polymers modified by radiation and peroxide treatment in the pre and post gel regions are shown in Figure 4 a) and b), respectively.

In Figure 4 a) it can be seen that molecular weight theoretical calculations agreed very well with the experiments both, before and after the gel point, for all radiation modified HPB samples. Besides some scattered values, radiation modification induces similar evolution of the molecular weight for HPB polymers regardless of their initial molecular weight or their irradiation conditions. In Figure 4 b), the experimental molecular weight data

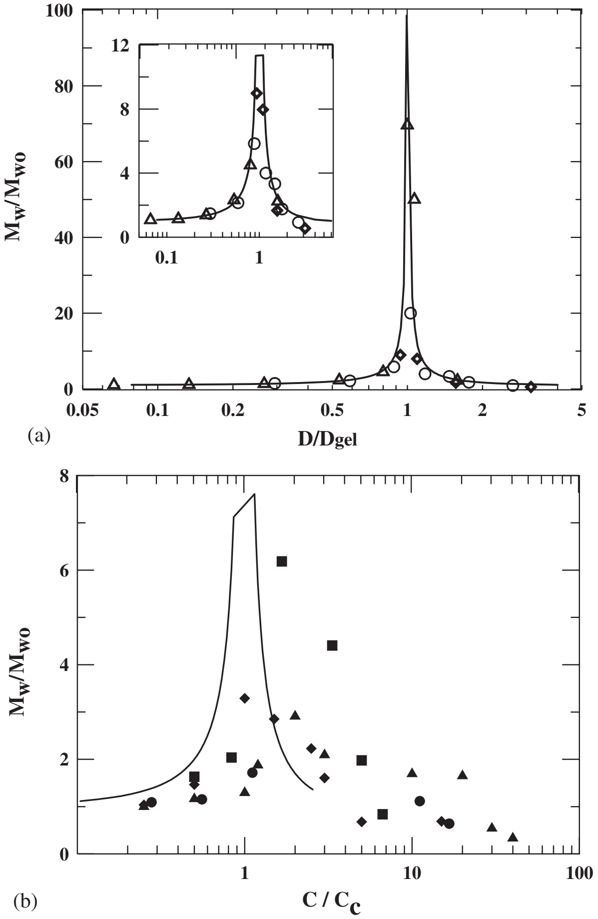


Figure 4.

a) Evolution of normalized weight average molecular weight of radiation modified HPB polymers as a function of the normalized radiation dose (D/Dgel). ***Reference***: (▬) theoretical prediction; (-) HPB-50 25 °C; (+) HPB-100 25 °C; (%) HPB-100 135 °C. b) Evolution of normalized weight average molecular weight of chemically modified HPB polymers as a function of the normalized peroxide concentration (C/Cc). ***Reference***: (▬) theoretical prediction; (■) HPB-29; (●) HPB-81; (◆) HPB-114; (▲) HPB-125.

for the modification with peroxide again follow the same tendency for all HPB polymers analyzed regardless of their initial molecular weight. However, in contrast with the polymers modified by radiation, these experimental data does not follow the expected molecular weight evolution predicted by the theoretical model. We could assume that the modification with peroxide has a particular chemical mechanism, possibly related with secondary reactions of the oxi-radicals, affecting the crosslinking efficiency during this modification process.

Rheological changes are a direct consequence of the induced modifications in the polymer molecular structure during the crosslinking process. Storage G′(ω) and loss G″(ω) moduli measurements at 177 °C were performed as a function of frequency, ω, for HPB-50 and HPB-45 polymers crosslinked by gamma radiation and by peroxide respectively.

Figures 5 a) and b) show the evolution of the rheological measurements with increasing doses of radiation or peroxide up to the gel point. The data corresponding to the original polymers exhibit the normal liquid-

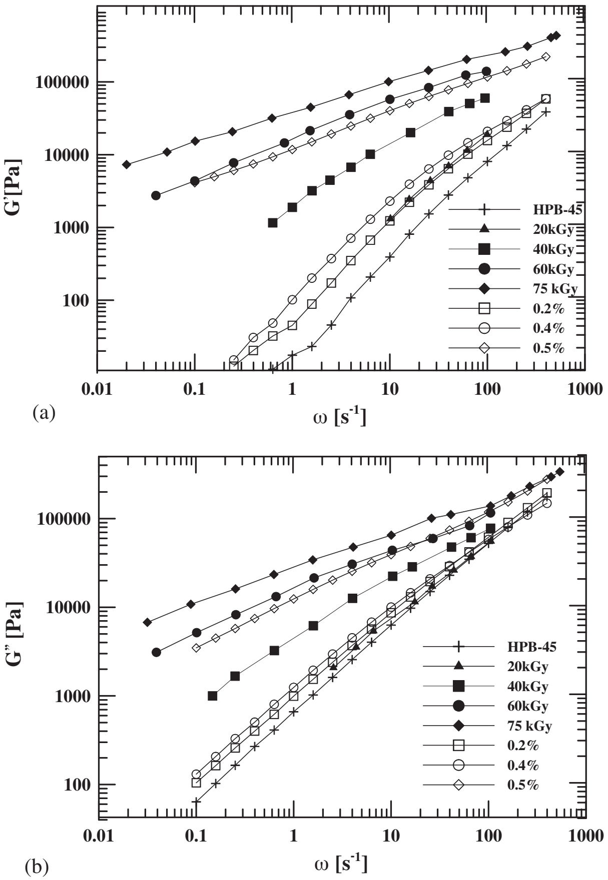


Figure 5.

a) Frequency dependence of the elastic modulus, G′(ω), for the chemically modified HPB-45 polymer and the radiation modified HPB-50 polymer, at 177 °C. b) Frequency dependence of the loss modulus, G″(ω), for the chemically modified HPB-45 polymer and the radiation modified HPB-50 polymer, at 177 °C.

like behavior of model linear polymer chains with slopes of 2 and 1 for G′(ω) (Fig. 5a) and G″ (ω) (Fig. 5b), respectively. The rheological response of the unmodified HPB-45 and HPB-50 was practically the same. Consequently the rheological changes observed during the modification of these polymers with increasing doses of radiation or peroxide should be representative of the main differences that these processes induce on the rheological behavior. As either of both types of modification is applied the G′(ω) curves show increasing relaxation times in the low frequency region. When the modified polymers get closer to the gel point, the G′(ω) and G″(ω) curves straighten over the entire frequency range with equivalent slopes of about 0.45.

Irrespective of the similarities mentionated above, clear differences are observed in the rate of evolution of both modification processes when the results are compared at equivalent doses relative to the critical dose for gelation. If we look for example to the rheological data obtained with a dose corresponding to about half of the critical one: close to 40 kGy for radiation and slightly higher of 0.2 wr% for peroxide modification, we observe that the evolution of the rheological properties is much more rapid in the case of irradiation than that obtained with the use of peroxides.The same observation is valid for the doses that correspond to 0.8 of the critical dose for gelation: 60 kGy and 0.4 wt% for radiation and peroxide respectively. Here, while the growth of the elastic modulus with radiation reaches values which are very close to those corresponding to the critical gel dose (75 kGy), those obtained by peroxide modification are still below to the values obtained by radiation with a dose equivalent to half of the critical value for gelation.

These differences indicate that the peroxide modification is not very efficient at low concentrations. Only at higher peroxide concentrations, close to those of the critical one for gelation, the evolution of the viscoelastic properties change rapidly reaching similar values to those obtained by irradiation. These differences are consistent with those observed in the evolution of the molecular weights in both processes at doses corresponding to the pre-gel region and with the differences observe in the evolution of the gel fraction in the post gel region. In all cases the evolution of the molecular and structural changes is more rapid when irradiation is employed. We still do not have a complete explanation for the differences observed in both processes, but part of the delays observed in the modification process with peroxide may be attributed to partial recombination, deactivation and secondary reactions that are known to be present when peroxides are employed.

4. Conclusions

We have investigated the chemical crosslinking by radiation and peroxy modificaton of ethylene-butene copolymers having narrow molecular weight distribution. Under the modification conditions adopted, it was found that the critical dose of radiation and concentration of peroxide necessary to reach the gel point decreases as the initial molecular weight of the crosslinked polymer rises. We found that scission is present in both modification processes at levels of about 5% of the molecular mass of the modified polymer. In the case of radiation, the evolution of the weight average molecular weight below the gel point and the fraction of gel and the molecular weight of the soluble fraction in the post gel region are accurately described by a theoretical model based on the classical assumptions of the network forming theories. However this theory fails to predict the evolution of the same molecular parameters when peroxide modification is employed. On the light of the present results the evolution of the changes induced by radiation seem to progress steadily and homogeneously with increasing doses all over the dose ranges explored in this study. The results obtained from the peroxide modification processes show that the evolution of the structural modification evolves at a considerable lower rate than that observed in the radiation results. Significant differences are also observed in the results obtained from both modification process in the post gel region. We are presently pursuing further experiments to explain the observed differences between them.

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