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Material Behaviour

Branching and rheological behavior after electron irradiation in metallocene ethylene-co-norbornene copolymers

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ABSTRACT

The effect of Electron beam (EB) irradiation on a cycloolefin copolymer based on ethylene and norbornene with intermediate molar content of norbornene has been evaluated. Crosslinking is not observed at any dose analyzed. Scission and branching of the chains simultaneously occur at low and high irradiation doses. Scission prevails for doses up to 167 kGy and, then, branching becomes dominant in the rheological bulk response at the highest dose. These side chains favor the development of reversible physical networks through entanglements and, accordingly, the G_N^0 value and the dynamic and zero-shear viscosities increase at high levels of irradiation compared with the same parameters found at smaller EB doses. The resulting structures attained after irradiation at different doses are inactivated to microorganism development and exhibit higher thermal stability and a broader temperature window for its standard applications in comparison with the pristine non-irradiated ethylene-co-norbornene (EN) copolymer.

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1. Introduction

The discovery of cocatalysts of the type methylaluminumoxane (MAO) was an important step for the development of metallocene catalysts, more than twenty years ago [1,2]. The most important characteristics of metallocenes are their single site properties that allow polymers (specially polyolefins) with narrow molecular weight distributions, polydispersity values being near two [2,3], to be obtained. Moreover, because of the possibility of controlling the microstructure in the final polymer [2,4,5], the use of these catalysts leads to synthesis of a very broad range of new materials. One of the best examples is the preparation of cycloolefins [6,7]. In particular, ethene-norbornene copolymers have received much attention

because of their attractive properties, being commercialized in 2000 by Ticona, Germany, under the trade name TOPAS. The different industrial grades are amorphous and, consequently, show high transparency and gloss. Their property profiles can be varied over a wide range by adjusting the chemical composition during polymerization. These new commercial materials exhibit a unique combination of properties whose performance benefits include: variable glass transition temperatures -from 65 °C up to 178 °C-, heat resistance, chemical resistance to common solvents, low moisture uptake, high water barrier, good mechanical properties, ease of extrusion and thermoforming, compatibility with polyolefins, excellent biocompatibility and inertness, among others. These numerous advantageous characteristics have made them widely accepted as packaging materials over a broad range of applications. Commercial grades comply with all major regulatory food contact requirements and, in addition, have passed biocompatibility protocols for their use

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in medical and pharmaceutical devices. Therefore, they must withstand a rigorous and complex sterilization process in order to ensure sterility and safety.

Several sterilization techniques exist for foods, medical devices and long-term implants. The common ones include sterilization through dry heat, steam, ethylene oxide and radiation. Electron beam, EB, sterilization is one of the most regularly used methods since a commercially successful technology has been developed and allows sterilizing a variety of foods and disposable medical devices with a wide range of densities in a very short time. Electron beam irradiation inactivates microorganisms either by causing microbial death as a direct effect of the destruction of a vital molecule or by an indirect chemical reaction. Upon irradiation, some chemical changes are induced in the excited polymeric material, including formation of free radicals, recombination and scission of bonds, cross-linking [8,9] and different oxidation reactions. The dose [10–12] and the atmosphere surrounding the material during radiation [11,13] have been reported to influence the extent of these mechanisms.

The present research deals with the effect of EB irradiation on a metallocene ethylene-co-norbornene copolymer. There are not too many articles in the open literature devoted to these interesting copolymers, those being primarily related to copolymers synthesized on a laboratory scale [14–21]. None of them, to the best of our knowledge, evaluates the influence of EB irradiation on a property as important as the rheological response. Therefore, several EB irradiation doses have been imposed, some of them much higher than those applied for sterilization to complement the study. The changes in structure have been checked by Wide-angle X-ray Diffraction, XRD, and Fourier Transform Infrared, FTIR; in glass transition temperatures by Differential Scanning Calorimetry, DSC; in thermal stability by Thermogravimetric Analysis, TGA; in molecular weights by Size Exclusion Chromatography, SEC, and in viscoelastic behavior at high temperatures by rheological measurements.

2. Experimental part

2.1. Material and film preparation

A commercially available metallocene ethylene-co-norbornene copolymer (EN), with trade name TOPAS 6013, has been used in the present research. It was supplied by Ticona, the technical polymers business of Celanese AG, and its characteristics are listed in Table 1.

Films were obtained by compression molding in a Collin press between hot plates (200 °C) at a pressure of 1.5 MPa for 4 min. A quench was applied to the different films from the melt to room temperature.

2.2. Irradiation of specimens

Electron beam (EB) irradiation was carried out at IONMED (an industrial installation) in atmospheric air at ambient temperature using a 10 MeV Rhodotron accelerator. All the polymeric films were irradiated on one side using a current of 5 mA such that the polymeric samples

Table 1

Characteristics of the commercial ethylene-co-norbornene copolymer analyzed.

Sample	Trade name	Norbornene	10^{-4}	$M_w/$	Density	MFI
		content	M_w	M_n		
		mol%	g mol^{-1}		g cm^{-3}	g 10 min^{-1}
EN	TOPAS 1630	48 ^a	10.9 ^a	1.97 ^a	1.02 ^b	13.0 ^b

^a Taken from reference [34].

^b Taken from Ticona Data Sheet. Density determination was performed under ISO 1183 and ASTM D792 norms whereas Melt Flow Index estimation at 260 °C under 2.16 kg by ASTM D1238 and ISO 1133 ones.

were exposed to an irradiation dose of about 33.6 kGy per pass. Several passes under these conditions were required for high irradiation doses. The EB irradiation doses are ranged throughout this work from 34 to 233 kGy, as reported in Table 2. The samples were labeled as EN-0, EN-34, EN-100, EN-167 and EN-233, the first being the non-irradiated specimen and the subsequent numbers referring to the experimental doses applied.

2.3. Sample characterization

Soxhlet extraction was performed for 24 h with hot toluene as solvent to determine the insoluble ratio of polymer chains. The weight fraction of gel, W_g in %, was calculated as:

$$W_g(\%) = W_g/W_0 \times 100 \quad (1)$$

where W_g is the weight of dry gel after extraction and W_0 is the initial weight of the dry gel.

Wide-angle X-ray diffraction (XRD) patterns were recorded in the reflection mode at room temperature using a Philips diffractometer with a Geiger counter, connected to a computer. Ni-filtered $\text{CuK}\alpha$ radiation was used. The diffraction scans were collected over a period of 20 min in the range of 2θ values from 3 to 43°, using a sampling rate of 1 Hz. The goniometer was calibrated with a silicon standard.

The IR spectra were obtained on films using a Perkin Elmer FTIR spectrometer equipped with an ATR device scanning between 600 and 4000 cm^{-1} ; 64 scans were accumulated for each specimen at a resolution of 4 cm^{-1} .

The characterization of thermal transitions was analyzed in a Perkin–Elmer DSC-7 calorimeter connected to a cooling system and calibrated with different standards. The sample weight ranged from 6 to 8 mg. The scanning rate used was 10 °C min^{-1} . The glass transition

Table 2

Nomenclature of different specimens, EB dose applied, glass transition temperature found in the first and second heating run (T_{g1}^{DSC} and T_{g2}^{DSC} , respectively) and degradation temperatures: onset temperature and that at which degradation is the largest (T^{onset} and T^{max} , respectively).

Specimen	EB dose kGy	T_{g1}^{DSC}	T_{g2}^{DSC}	T^{onset}	T^{max}
		°C	°C	°C	°C
EN-0	0	135	134	400	494
EN-34	34	144	143	450	513
EN-100	100	144	143	440	514
EN-167	167	143	141	450	514
EN-233	233	145	142	445	518

temperature, T_g , was determined as the temperature at which the specific heat increment is half of the total at the transition.

The thermal stability (onset temperature of degradation and that at which degradation is the largest, T_{onset} and T_{max} respectively) was estimated by thermogravimetry using a Perkin–Elmer TGA7 equipment working under an inert atmosphere. The equipment was calibrated according to standard protocols. The sample weights ranged from 4 to 6 mg, and the heating rate was $10\text{ }^\circ\text{C min}^{-1}$.

The molecular weights and molecular weight distributions for the different irradiated specimens at particular doses were obtained by Size Exclusion Chromatography (SEC) using a Waters 150-C ALP/GPC equipped with a set of three $20\text{ }\mu\text{m}$ PL-GEL MIXED-A columns from Polymer Labs. The solvent used was 1,2,4-trichlorobenzene (TCB) at $135\text{ }^\circ\text{C}$ 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 linear polyethylene [22].

Additional molecular information (molecular weights and molecular weight distributions, branches number per molecule and branches frequency per 1000 carbon atoms) was obtained for the different irradiated specimens at particular doses by Size Exclusion Chromatography (SEC) using a Viscotek/GPC equipped with four detectors in series, one for refractive index determination, another for intrinsic viscosity estimation and two light scattering detectors. The solvent used was toluene at $80\text{ }^\circ\text{C}$ with 0.8 mL/min flow.

The rheological characterization was carried out in small-amplitude oscillatory shear mode using a rotational rheometer from Rheometrics Inc. (Rheometrics Dynamic Analyzer RDA-II). The tests were performed using parallel plates of 25 mm in diameter, at a frequency range between 0.1 and 500 rad/s , and a temperature range of 170 – $250\text{ }^\circ\text{C}$. All tests were carried out at small strains in order to assure the linearity of the dynamic responses [23]. The series of frequency sweeps were repeated twice with the same sample at different strains in the range of linear viscoelasticity. Excellent agreement between these results was found in all cases.

3. Results and discussion

Measurements for determination of gel content by soxhlet extraction revealed that the different specimens are completely soluble independently of the irradiation dose imposed within the empirical range analyzed. Therefore, EB irradiation does not lead to formation of gel structures in this EN copolymer. This feature seems to be associated with the presence of a small phenolic antioxidant (Irganox 1010®) content, which is incorporated in the polymer provided by Ticona, as described in a previous publication for a copolymer with similar norbornene content [24]. The addition of hindered phenol antioxidants, such as Irganox 1010®, is reported to minimize crosslinking as well as chain scission reactions [25,26]. On the other hand, the extent of its effect is also dependent on the chemical nature of the polymeric material and, particularly in these EN copolymers, on ethylene composition. It is known and

reported for polyethylene [27] that crosslinking mechanism takes place from low doses, becoming predominant at doses higher than 120 kGy . Following this line, an insoluble fraction of around 65% has been determined at a dose of 150 kGy in an EN copolymer with ethylene molar fraction higher than that exhibited by the copolymer under study, although that copolymer was entirely soluble at lower doses [24]. By contrast, the results found in another EN industrial grade with higher norbornene content and irradiated in air with gamma rays [28] are in agreement with our results, *i.e.*, the non-presence of an insoluble fraction. Accordingly, the presence of antioxidants is important to suppress crosslinking and, consequently, gel structures in EN copolymers at intermediate and high norbornene contents.

The DSC experiments performed to evaluate the thermal properties of the original EN copolymer (TOPAS 6013) and their irradiated counterparts are shown in Fig. 1. The thermograms reveal that the original EN copolymer exhibits a unique thermal transition: its glass transition, T_g . This fact corroborates its amorphous nature ascribed to its relatively high norbornene content. The effect of EB irradiation on T_g is rather significant independently of the dose applied. A shift to higher temperatures is observed and, thus, the glass transition is moved from $135\text{ }^\circ\text{C}$ to about $144\text{ }^\circ\text{C}$ for all the irradiated specimens, as reported in Table 2. This displacement of T_g seems to indicate that mobility is reduced because of the EB irradiation.

The observed displacement of T_g on the irradiated specimens persists after a second heating cycle performed by first cooling the samples from well above T_g to room temperature at $10\text{ }^\circ\text{C/min}$ and then heating up again at the same rate beyond the glass transition temperature. As the EN copolymer was irradiated at room temperature, this second run was performed to verify that the reported T_g 's were not affected by the possible presence of unreacted macro-radicals trapped in the glassy structure of the polymer. If this effect were present, additional micro-structural changes should be observed once the polymeric chains gain mobility above their glass transition, *i. e.*, in their elastomeric-like state. The results reported in Table 2 show that second heating T_g values are rather similar to

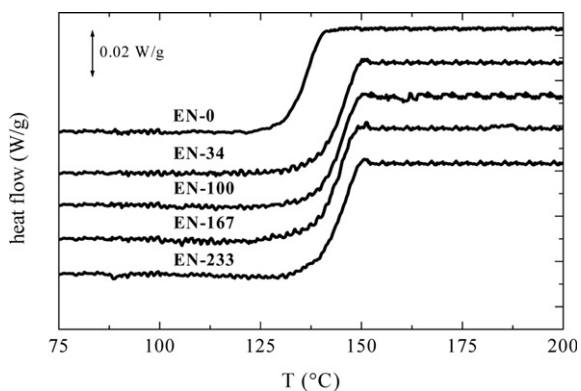


Fig. 1. DSC first heating curves for the pristine EN copolymer and the irradiated specimens at different doses, at $10\text{ }^\circ\text{C/min}$.

those found during the first run for the lower irradiation doses and slightly lower for doses above 167 kGy. These results indicate that irradiation leads to a mobility reduction in the solid state of the irradiated EN specimens.

At this point, we would like to discuss the intriguing results referred to the apparent invariance of the glass transition temperatures with the irradiation dose applied to the EN copolymer within the dose range covered by this work. As is well known, EB radiation of polymers may induce crosslinking, scission or reaction of the formed macro-radicals with other species such as air, monomers or functionalizing agents. In our case, the development of crosslinking by EB would validate this mobility hindrance and the subsequent T_g shift to higher temperatures. Even though the extent of crosslinking induced in the irradiated EN copolymers was not sufficient to induce gelation, - as revealed by the fact that an insoluble fraction was not found on any of the performed soxhlet extractions - the formation of branched species was present as was inferred from the rheological experiments discussed later. If this was the only structural factor affecting T_g , a temperature displacement towards higher values of this property should be expected with increasing crosslink density, as observed in other polymers [29].

The results from SEC and rheology exposed below also show that chain scission reactions are taking place as a consequence of the irradiation process. This should induce a shift of T_g towards lower temperatures due to the increase in free volume generated by a higher concentration of chain ends [30]. Additionally, formation of oxidized polar groups due to irradiation occurs, as detected by FTIR analysis, whose content increases with dose. This may lead to additional interchain interactions that will have an effect on T_g . All of these experimental results seem to indicate that the observed evolution of T_g with irradiation is the result of a complex interplay between changes in molecular weight, MWD , chain branching and polar group content generated by this process.

On the other hand, XRD measurements were performed to get further knowledge of the effect of EB dose on the polymer structure. As aforementioned, the EN copolymer under study is amorphous and the appearance of crystalline diffractions is not expected as a result of EB irradiation. However, some micro-structural changes might induce the recombination of broken chains with subsequent formation of norbornene sequences, these being observable by XRD profiles. The polynorbornene homopolymer displays a characteristic pattern with two amorphous halos [17]. Accordingly, the presence of a prominent peak at low angles at similar location to that exhibited by polynorbornene (at around 10° in a 2θ representation) should be evidence of the presence of blocks of three or more norbornene sequences within the backbone in ethylene-co-norbornene copolymers. The XRD patterns show a single amorphous halo in the non-irradiated EN-0 specimen. This result points in favor of the efficiency of the catalytic system used for the copolymerization that makes possible the random distribution of norbornene units along the chain in this copolymer and, therefore, the non-presence of norbornene block sequences. The XRD results show no evidence of any peak at low angles in the EB irradiated samples. This is an indication that no significant changes occur on the microstructure of the EN copolymer. In addition, the location of the amorphous halo is almost constant for the different specimens irrespective of the applied EB dose. This fact indicates that the intermolecular distance of macromolecular chains does not change with irradiation.

Supplementary and more significant microstructure information can also be attained from FTIR experiments. Fig. 2 shows that the non-irradiated EN-0 copolymer exhibits two strong vibrations at around 2850–2970 and 1340–1470 cm^{-1} , both associated with the alkyl groups, as well as one weak vibration at around 1610–1680 cm^{-1} related to alkene groups [31]. The vibrations at longer wave number are ascribed to the symmetric and asymmetric tensions of $-\text{CH}_2-$ groups, respectively, whereas those at 1340–1470 cm^{-1} correspond to $-\text{CH}_2-$ flexions. The

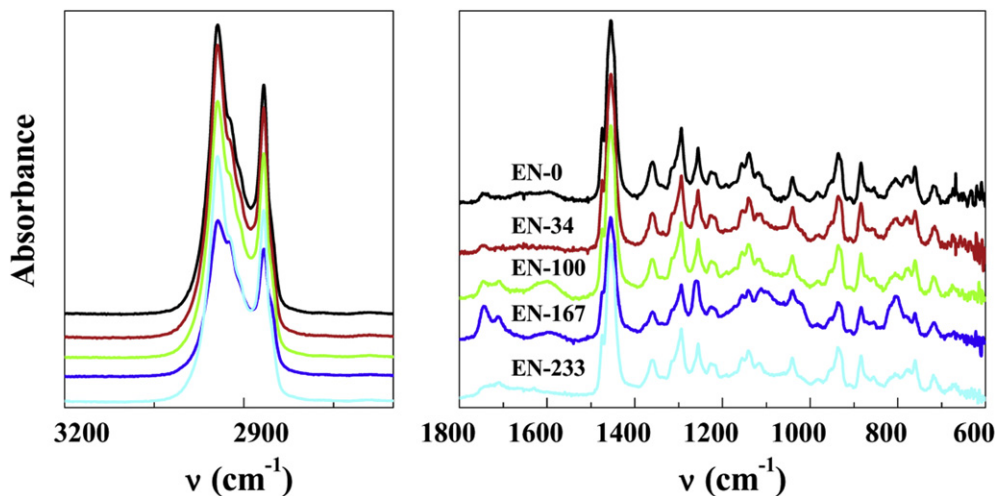


Fig. 2. FTIR absorption spectra at room temperature for the different specimens irradiated at distinct doses compared with that exhibited by the initial EN copolymer. From top to bottom: EN-0, EN-34, EN-100, EN-167 and EN-233.

other signals below those commented on are considered as fingerprint characteristic of these EN copolymers. As previously remarked, EB irradiation might lead to the formation of free macro-radicals and their further evolution can cause either chain scission or chain branching. Fig. 2 depicts the variation observed in the alkyl groups' vibration at 1460 cm^{-1} , especially important at the highest doses. Consequently, the normalized intensity observed at 233 kGy is much higher than that presented at 167 kGy. At around $1700\text{--}1750\text{ cm}^{-1}$ new bands appear related to the formation of ketones, lactones and hydroperoxides derived from application of EB irradiation, as well as another band at about 1600 cm^{-1} , this last one indicating development of unsaturations [32]. These new vibrations indicate that some oxidative species have been generated by the irradiation process and might lead to the physical interactions discussed in the previous paragraphs. The formation of these oxidative species is favored since the irradiation process took place in atmospheric air, although its extent is reduced because of the presence of hindered phenolic antioxidant. The effect that EB irradiation has on the formation of oxidized species in the EN copolymer is displayed in Fig. 3. It shows the evolution of the ratio A_{1720}/A_{1460} , *i. e.*, between the normalized absorbance of the vibration at 1720 cm^{-1} associated with different types of carbonyl groups created during the irradiation process and that at 1460 cm^{-1} related to the flexion mode of the methyl groups. The growth of the concentration of the oxidized species reveals an almost exponential variation of this ratio, at least on the surface and up to a depth of few microns for each specimen. We also attribute the partial discoloration observed in specimens irradiated at the highest doses to the partial oxidation of the alkyl groups. All these results prove that oxidation and alkene forming mechanisms occur simultaneously during irradiation independently of dose.

To obtain additional information about other processes induced by irradiation such as chain scission, crosslinking and variations in molecular weight and molecular weight distributions, size exclusion chromatography was performed on the initial EN-0 copolymer and the irradiated specimens. It has to be said that the empirical protocol used, detailed in the Experimental Section, makes only

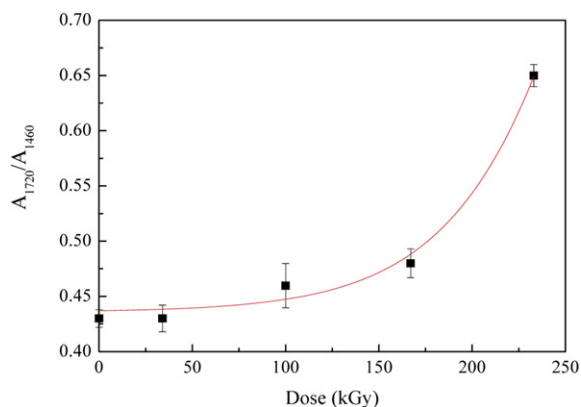


Fig. 3. Ratio of absorbance at 1720 cm^{-1} band to that found at 1460 cm^{-1} for the samples irradiated at different doses.

Table 3

Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity (M_w/M_n) determined from SEC measurements as well as zero-shear viscosity (η_0) and plateau modulus (G_N^0) values obtained from rheology experiments.

Specimen	M_n	M_w	M_w/M_n	η_0	G_N^0
	g mol^{-1}	g mol^{-1}		Pa s	Pa
EN-0	27,700	48,900	1.76	10,50,000	3,54,000
EN-34	25,700	44,900	1.75	7,30,000	3,21,000
EN-100	17,500	46,000	2.63	6,60,000	2,34,000
EN-167	15,000	47,000	3.14	–	1,20,000
EN-233	15,800	88,300	5.57	–	2,76,000

qualitative estimations of the molecular weights. Standard SEC is a technique based on the separation of diluted polymer molecules by their hydrodynamic volume and, then, the average molecular weights of the irradiated samples are underestimated because the typical calibration curve is only valid for linear molecules. Nevertheless, SEC is still very useful to visualize the major changes occurring in the molecular weight and molecular weight distribution of the polymer molecules when increasing doses of radiation are applied.

The values of the estimated molecular weights based on the linear calibration are reported in Table 3. After application of a 34 kGy dose, a slight decay of the molecular weight is observed. Then, with increasing radiation up to doses of 167 kGy, a continuous decay in the number average molecular weight is observed, indicating the increment of low molecular weight species. Beyond this dose, the weight average molecular weight begins to grow significantly towards values that considerably exceed the molecular weight of the original polymer. Moreover, the molecular weight distribution increases continuously through the whole process of irradiation from an initial value of 1.76 to a final value of 5.57 obtained with a dose of 233 kGy. These

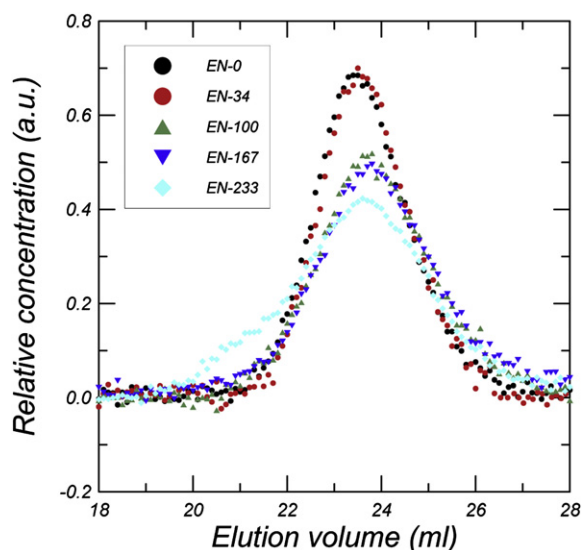


Fig. 4. Molecular weight distribution curves by SEC of the initial EN copolymer and the soluble fractions of the irradiated specimens.

features indicate that scission and recombination of chain segments to develop branched structures are both taking place at different stages of the irradiation process. Fig. 4 shows the superimposed normalized SEC chromatograms of the original and irradiated EN samples. Depending on the irradiation dose, different displacements are observed on the chromatograms at the low and high molecular weight side, which are useful to understand the above reported results. At low levels of irradiation, the main changes with respect to the chromatogram of the original EN-0 specimen appear at the low molecular weight tail, which corresponds to the higher elution volumes. This is a consequence of the chain scission reactions that induce the formation of molecules with masses lower than those that belong to the original EN-0 copolymer. The other side of the chromatograms corresponds to high molecular weight species that may be present as a consequence of the combination of macro-radicals formed during the radiation process. In this step, two macro-radicals react to generate the branched macromolecules of higher mass. With doses below 167 kGy, the growth of a significant amount of high molecular weight branched species is difficult to detect by SEC. This technique is not quite suitable to discern low amounts of chain branching [33]. Accordingly, no conclusive results with respect to this point can be obtained exclusively from the analysis of chromatograms represented in Fig. 4. However, the reported results that show an increase in T_g values of the irradiated specimens and the rheological behavior, which will be commented on later in the text, are consistent with the presence of a significant branching content even at low radiation levels.

At the highest doses, the fraction of high molecular species increases. Therefore, beyond 167 kGy, the fraction of high molecular weight molecules becomes more evident than the one at the low molecular weight side of the chromatogram. In spite of the limitations of the technique to detect low levels of chain branching, the outcome of the SEC results is accurate enough to confirm that the radiation process generates competition between chain-branching and chain-scission for this particular system, although the former process seems to become dominant at the highest doses.

To corroborate this aspect, SEC measurements using equipment with higher performance was utilized. Table 4 summarized the results found. In addition to molecular weights and molecular weight distributions, this equipment allows determination of the number of branches per

Table 4

Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity (M_w/M_n) determined from SEC measurements as well as zero-shear viscosity (η_0) and plateau modulus (G_N^0) values obtained from rheology experiments.

Specimen	M_n	M_w	M_w/M_n	br. nbr. ^a	br. fr. ^b
	g mol ⁻¹	g mol ⁻¹			
EN-0	41,600	70,800	1.70	–	–
EN-34	27,200	68,300	2.51	0.072	0.036
EN-100	30,900	1,07,800	3.49	3.52	0.87
EN-167	35,700	1,01,400	2.84	3.21	0.76
EN-233	49,400	1,62,100	3.28	5.58	1.57

^a Branches number per molecule.

^b Branches frequency per 1000 carbon atoms.

molecule and branch frequency per 1000 carbon atoms, providing quantitative data of the fact that chain-branching becomes more and more important as irradiation dose increases.

The viscoelastic properties of the original EN-0 sample and those of the EB irradiated counterparts were examined by dynamic shear rheology at different temperatures. The results obtained at temperatures between 170 and 250 °C for the EN-0 copolymer are shown in Fig. 5 in the form of a van Gurp–Palmen (vG-P) plot, where the phase angle δ is plotted against the absolute value of the shear complex modulus G^* . In this kind of representation, all the isothermal frequency curves of a thermorheologically simple material merge into a common contour. Moreover, in the absence of long chain branching, this type of plot evolves from high towards low G^* values passing through a minimum of the phase angle δ at the point where the complex modulus equals the value of the plateau modulus, G_N^0 . After reaching its minimum value at G_N^0 , the complex modulus raises again passing through an inflection point to reach a final plateau at $\delta \cong 90^\circ$, where the terminal flow region is attained.

The rheological response of the original EN-0 specimen corresponds to the type of material just described. In this case, the minimum in G^* is located at $\sim 354,000$ Pa, which corresponds to the G_N^0 value of an EN copolymer with 48% norbornene content. This result is in good agreement with previous works reported by K. Thorshaug [14] et al. and J. Y. Shin et al. [34] on linear EN copolymers with norbornene molar content of 46% and 48%, respectively. In addition, confirming the X-ray diffraction patterns commented previously, the particular type of evolution of the EN-0 copolymer in the Van Gurp–Palmen plot is characteristic of a fully amorphous polymer since the G^* minimum in semicrystalline polymers, like for example common polyolefins, is not observable because crystallization normally occurs at the low temperatures required to reach that part of the data representation.

On the other hand, time-temperature superposition data of the EN copolymers dynamic viscosities, η' , over seven decades of time are shown in Fig. 6 at a reference temperature of 190 °C. The value of η' for the neat EN-0

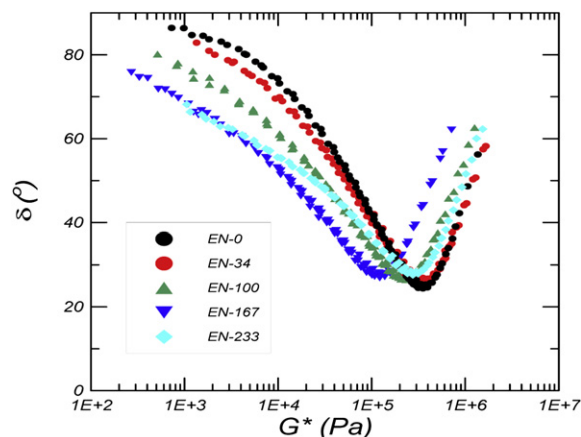


Fig. 5. Van Gurp–Palmen plot for the different samples.

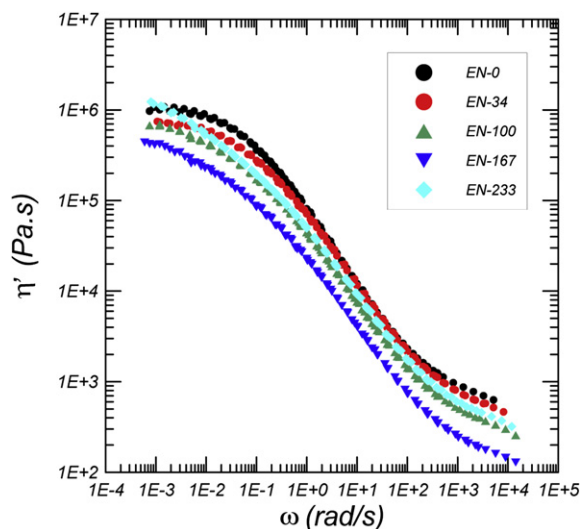


Fig. 6. Master curve of dynamic viscosity versus frequency at the reference temperature of 190 °C for the different specimens.

resin evolves from the low frequency region, where $\eta_0 = 1,050,000$ Pa s, passing through the power law region to finally approach the region of the second Newtonian plateau at frequencies above 10^3 rad/s.

The irradiation of the original EN copolymer leads, as already discussed with reference to the evolution of T_g and the SEC results, to scission and branching reactions that affect the rheological properties of the original polymer. A dose as low as 34 kGy does not significantly influence the value of G_N^0 of the original copolymer since the minimum in the vGP-plot is found, within experimental error, at almost the same locus as the un-irradiated EN-0: $G^* \sim 321,000$ Pa. However, careful comparison of the evolution of the rheological results of EN-0 and EN-34 in Figs. 5 and 6 shows distinct differences between them: First, the minimum at G_N^0 for EN-34 in Fig. 5 is attained at a higher value of the shift angle δ . This is in agreement with the SEC results, the expected response for a polymer of lower molecular weight than the original EN-0 copolymer [35]. Secondly, the value of η_0 in the dynamic viscosity plot in Fig. 6 decreases from the $\eta_0 = 1,050,000$ Pa s obtained for EN-0 to $\eta_0 = 730,000$ Pa s for EN-34, which point in the same direction. These results confirm that scission is present at the lowest radiation levels covered by this work. They also demonstrate the superior sensibility of the rheological measurements with respect to SEC to detect low degrees of modification of the chain structure of the polymer by either scission or crosslinking. While SEC measurements were able to show only very slight differences between EN-0 and EN-34, the rheological data allowed clear differentiation between them.

A third distinction is also observable on the Van Gurp–Palmen plot for EN-0 and EN-34. For a given angle δ , there is a clear shift of the rheological data from EN-34 at the left flank of the plot towards lower G^* values. According to the results obtained by Trinkle and Friedrich [35,36] from the study of several tailor-made polymers with different structures, this shift may be a consequence of

increasing polydispersity and/or branching. As the SEC results do not reveal enlargement of the molecular weight distribution, the changes observed in the rheological behavior are most probably due to an incipient concentration of branches that are generated in the polymer by radical recombination reactions. All this information supports the thought that at low levels of radiation both processes –scission and branching– are present to certain extent, but the effect of scission on the rheological behavior predominates in the molten state.

Increasing the radiation dose to 100 kGy shifts the entire vG-P plot to the left, towards lower G^* values, and slightly upwards. G_N^0 is now located at $G^* \sim 234,000$ Pa. The shift in the direction of lower G^* is mainly a consequence of the diluting effect induced in the EN-100 specimen by the presence of low molecular weight molecules that appear through scission reactions which are clearly detected at this level of radiation by SEC. The location of the minimum of G^* at higher values of the shift angle δ is a rheological consequence of the lower molecular weight of the irradiated polymer. The dynamic viscosity results also shifted towards lower η' values over the entire frequency range. The clear change of the SEC towards higher elution volumes and the widening of the whole chromatogram shown in Fig. 4 for this dose of irradiation support these results. At 167 kGy, the same tendency is observed and, consequently, a displacement of the minimum value on G^* to 120,000 Pa is found. Finally, recombination reactions seem to prevail over scission in the EN-233 sample, shifting the minimum of G^* to 276,000 Pa. At this point, the vGP-plot undergoes a slower evolution of the G^* values from the minimum towards the terminal flow region. This is distinctive of the presence of long branches. Also, the dynamic viscosity curve shows a shift to higher η' values over the entire frequency range. In addition, the evolution of η' toward the zero-shear viscosity at the lower frequencies is clearly affected, indicating the existence of a significant amount of branches. The SEC corresponding to the EN-233 sample with the highest irradiation dose also indicates, in support of these observations, considerable enlargement of the concentration of molecules of high molecular weight which result from the long-branched macrochains.

To obtain some information about the thermal stability of the existing species, thermogravimetric measurements have also been performed. The values of the temperature at which the degradation process starts, T^{onset} , and that at which degradation is the greatest obtained from the derivative, T^{max} , are reported in Table 2. The results obtained indicate that independently of the applied irradiation dose, the thermal stability is higher than that exhibited by the non-irradiated EN-0 sample. The location of both temperatures is also rather independent of the EB dose. Therefore, the resultant branching structure is thermally more stable than that existing in the initial EN sample.

4. Conclusions

The effect of Electron beam irradiation has been studied in a cycloolefinic ethylene-co-norbornene copolymer with intermediate molar content of norbornene over a wide EB dose range. An insoluble gel fraction was not found in this

EN copolymer independently of irradiation dose within the wide range analyzed. Gelation was then suppressed, probably due to the presence of hindered phenolic antioxidant incorporated in the original EN-0. However, scission, oxidation and branching processes are simultaneously occurring within the whole range of irradiation analyzed. SEC measurements performed on solutions of irradiated specimens show that scission predominates for low doses whereas macroradical recombination mechanisms and, consequently, branching becomes dominant at doses higher than 167 kGy. Rheological response of the molten bulk is also dependent on EB dose. G_N^0 values, dynamic and zero-shear viscosities decrease as dose increases up to 167 kGy. For the highest irradiation dose, these rheological parameters increase indicating the great importance in the molten state of the existence of entangled branched structures that predominate over the effects of chain scission. The investigation has also highlighted that this EN copolymer exhibits good irradiation resistance to typical sterilization dose (lower than 50 kGy) when used as material for packaging, medical and pharmaceutical devices. Moreover, glass transition temperature and thermal stability of solid films is even shifted to higher temperatures independently of dose applied. Accordingly, the temperature window for its standard applications is slightly enlarged because of irradiation.

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