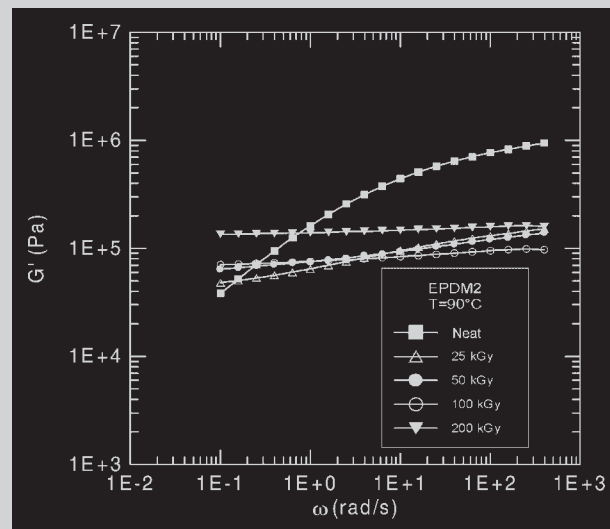


Summary: Two metallocene EPDMs with the same weight fraction of ethylene but differing in diene content were cross-linked, either by dicumyl peroxide (DCP) or β -radiation. The effect of different diene and propylene content on the molecular structure and the mechanical properties once the materials were crosslinked was studied. The final gel content was very high due to the large level of unsaturations. The crosslinking process was monitored by FTIR spectroscopy by following the decay of unsaturations and the variation of the carbonyl groups that are related to the oxidation grade. It was found that β -radiation crosslinked samples exhibited a lower oxidation grade than those crosslinked by DCP. An oscillant disc rheometer was employed to follow the evolution of the rheological properties, the scorch time, and the time corresponding to full cure during the crosslinking reaction with DCP. In addition, in order to characterize the state of cure we have studied the rheological properties in shear employing a dynamic parallel plate geometry. These results were correlated with those obtained from the molecular characterization of the soluble fraction by size exclusion chromatography. The experiments indicate that, at low irradiation doses, there is a high rate of chain scission reactions that cause an important decrease in storage modulus. Whereas, at high irradiation doses the rate of chain scission reactions diminishes, thus the storage modulus increases but it still remains at lower levels

than those corresponding to the original terpolymers. The tensile properties, hardness (Shore A) and compression set tests also suggest the presence of chain scission reactions.



Storage modulus (G') versus frequency for a β -irradiated sample.

Characterization of Metallocene Epdm Terpolymers with High Diene and Propylene Content Crosslinked by Dicumyl Peroxide and β -Radiation

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Introduction

The development of metallocene catalysts permits the production of new ethylene copolymers and terpolymers with promising better mechanical properties. These polymers are characterized for their regular structure and homogeneous comonomer distribution. They have a wide range of applications, some of them in the automotive industry. But, for certain purposes, they need to be crosslinked in

order to achieve a good balance in their properties at high temperatures.^[1–3] Ethylene-propylene-diene terpolymers (EPDM) have been recently emerging as a dominant elastomer in several engineering applications, particularly in applications that demand excellent chemical and thermal stability.^[4] Polymers containing unsaturated groups, such as dienic elastomers are well known for their potential to be crosslinked. High diene contents provide very fast crosslinking cycles, which are of great interest for the industry.^[5]

In order to obtain amorphous terpolymers with an elastomeric behavior and a good elastic recovery, EPDM terpolymers are polymerized with high propylene content.^[6,7]

β -Radiation crosslinking is a well established industrial process. Nowadays, over 800 electron beam plants are in operation in the treatment of polymer products in the world.^[8] Under the action of β -radiation ethylene-propylene elastomers are able to crosslink, attaining proper crosslinking levels with minimum degrees of oxidation.^[8–11]

Therefore, in this study we focus on the characterization of metallocene EPDMs crosslinked by a typical and well-known method, such as peroxide initiation, and we compare those results with those obtained by β -radiation.

Experimental Part

The materials used were two metallocene EPDM grades supplied by DuPont-Dow Elastomers: NORDEL IP 4570 (EPDM-1), Mooney viscosity 70 and NORDEL IP 5565 (EPDM-2), Mooney viscosity 65, with 5 wt.-% and 7 wt.-% ethylenenorbornene (ENB) respectively, (Table 1). The organic peroxide used in this work was Dicumyl Peroxide (DCP) (99% purity) as a crystalline powder recrystallized from methanol. It was supplied by Atofina.

Compression molded samples of the original polymers were irradiated in air by an electron beam accelerator (model Rhodotron TT200, 10 MeV), with irradiation doses ranging from 0–200 kGy. The radiation doses were chosen in the region ranging from 25–200 kGy, which is that of technical interest from the point of view of the properties of the materials. For the peroxide crosslinking experiments, different amounts of DCP (0.5–10 phr) were dispersed in the original EPDMs employing a Leistritz co-rotating twin-screw extruder at 85 °C, 55 rpm and 2 kg/h of mass flow rate. Finally, compression molded samples of the mixture were crosslinked at 190 °C under a pressure of 30 MPa.

The size exclusion chromatography (SEC) measurements were performed in a Waters 150-C ALP/GPC instrument, equipped with a set of three 20 μ m PL-GEL MIXED-A columns from Polymer Labs in series with a MALLS spectrophotometer Dawn DSP (Wyatt Tech. Co.), laser He-Ne (632.8 nm). The solvent used in these experiments was 1,2,4-trichlorobenzene (TCB) at 135 °C with 1 mL/min flow. The molecular weights of the polymers were estimated following the standard calibration procedure using monodisperse polystyrene samples and the corresponding Mark-Houwink coefficients for polystyrene and linear polyethylene in TCB.^[12,13] The corresponding coefficients for EPDM in TCB were not

found in the bibliography, so the molecular weights must be only considered qualitatively.

FTIR analysis was carried out on a Bomem (Hartmann & Braun) Model NB-150 mounted on a Golden Gate ATR accessory, with a 4 cm^{-1} resolution and 64 scans. Samples were 2 mm thick.

The rheological characterization of all materials was carried out in small-amplitude oscillatory shear flow geometry using a rotational rheometer from Rheometrics Inc. (model RMS-605). The tests were performed using parallel plates of 25 mm in diameter, at a frequency range between $5 \cdot 10^{-2}$ and $5 \cdot 10^3$ rad/s, and a temperature range of 30–90 °C. All test were carried out at small strains in order to guarantee the linearity of the dynamic responses.^[14] Several of the series of frequency sweeps were repeated twice with the same sample. Excellent agreement between the results was found in all cases, indicating that no measurable degradation occurred during the rheological tests.

The gel content was determined in boiling xylene according to the ASTM D2765-95, compression set tests were made according to the UNE-EN ISO R 815, the Shore A hardness tests according the UNE-EN ISO 868, and tensile tests were performed according to the UNE-EN ISO 37 standard methods. Differential scanning calorimetry (DSC) curves were recorded on a Mettler Toledo DSC 821/400 instrument at a heating rate of 10 °C/min. An EEKONER oscillating disc rheometer (ODR) recorded the curing curves at 190 and 155 °C, 3 ° amplitude and 1.7 Hz frequency.

Results and Discussion

Characterization of the Original Metallocene EPDM Terpolymers

The molecular characterization by SEC and MALLS shows that both terpolymers have a relatively narrow molecular weight distribution and that EPDM-1 has a higher molecular weight than EPDM-2. These results are in good agreement with the values of Mooney viscosity reported by the supplier (Table 1).

The elastic, $G'(\omega)$, and loss dynamic modulus, $G''(\omega)$ for both EPDM terpolymers was measured as a function of frequency. In order to analyze the rheological behavior of the original polymers in a wider range of the frequency spectrum we carried out a time-temperature superposition shift in the range of temperatures between 30 and 90 °C. Steps of 10 °C were employed fixing the reference temper-

Table 1. Characteristics of EPDM terpolymers from supplier and molecular characterization by MALLS and SEC.

Material	ENB	Ethylene/ Propylene	Mooney viscosity ML 1 + 4, 125 °C	MALLS			SEC		
	wt.-%	wt.-%		\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
				g/mol	g/mol		g/mol	g/mol	
EPDM-1	5	50/45	70	129 000	218 000	1.69	78 400	180 000	2.30
EPDM-2	7	50/42.5	65	116 000	201 000	1.73	77 500	168 000	2.17

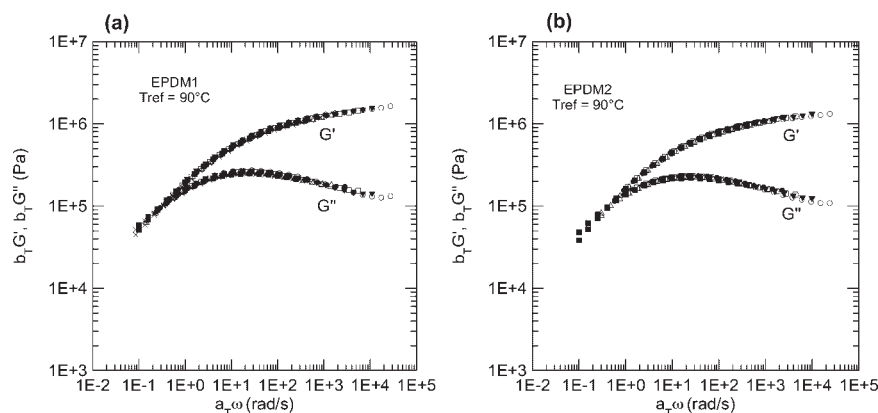


Figure 1. Master curves: storage modulus, loss modulus, dynamic viscosity $(b_T/a_T)\eta'$ and $\tan \delta$ versus frequency at the reference temperature of 90 °C. a,b) EPDM-1; c,d) EPDM-2.

ature at 90 °C. Two parameters can be obtained through the time-temperature superposition principle:^[14,15] the frequency shift factor a_T and the modulus shift factor b_T . Then, it is possible to build the master curve at 90 °C for both terpolymers by plotting $b_T G'(\omega)$, $b_T G''(\omega)$ and $\tan \delta = G''/G'$ versus $a_T \omega$. The master curves have been obtained using the IRIS software,^[16] which has extended the frequency range of our measurements by approximately two decades. Figure 1 shows that the values of $G'(\omega)$ for EPDM-1 in the intermediate and terminal regions are slightly higher than those of EPDM-2. This is consistent with the differences in molecular weight between those polymers.

For materials far from the glass-transition temperature, such as polyolefins in the molten state, the temperature dependence of a_T is usually described by an Arrhenius expression or by the Williams-Landel-Ferry (WLF) expression.^[17] We used the Arrhenius expression, which is the best equation that fits experimental data at high temperatures:^[18]

$$a_T = \exp \left[\frac{\Delta H'_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (1)$$

where $\Delta H'_a$ is the flow activation energy, T is the absolute temperature, T_0 is the absolute reference temperature and R is the universal gas constant. The flow activation energy is strongly dependent on the molecular parameters of the polymers and the relaxation mechanism. The close values found for the activation energies of both copolymers, $\Delta H'_a = 25.8$ kJ/mol for EPDM-1 and $\Delta H'_a = 26.4$ kJ/mol for EPDM-2, confirms that the molecular structure of both EPDM terpolymers is very similar.^[19]

Characterization of the Crosslinked EPDM Terpolymers

Molecular Characterization

The soluble fraction of β -radiation crosslinked samples after the gel point was extracted by xylene and was analyzed by SEC combined with MALLS, determining \bar{M}_w and \bar{M}_n .

The corresponding SEC data describing the molecular weight distributions (MWD) of the soluble fractions are displayed in Figure 2. It can be seen how the curves shift to higher elution volumes (lower molecular weights) with increasing irradiation doses. Moreover, at intermediate radiation doses the SEC data show a bimodal distribution of species, with a low molecular weight tail that grows significantly as the irradiation doses increase, and merges to a wide main single peak of low molecular weight at the maximum dose of 200 kGy.

In the post-gel region, beyond of the critical dose of gelation, the decrease in molecular weight of soluble fractions with increasing irradiation doses is very important. Close to the gel point, the soluble fraction is composed by a complex mixture of highly polydispersed and highly branched molecular species but, as the radiation doses is increased, the selective incorporation to the gel of those molecules with the uppermost molecular weight causes a significant reduction in the molecular weight and the polydispersity of the soluble fraction.

There is a complex mechanism caused by β -radiation, which involves crosslinking and chain scission, especially in the post-gel region, and consequently \bar{M}_w and \bar{M}_n molecular weights of soluble fractions decrease from the values of the original terpolymers. Two factors are responsible for this response: 1) chain scission due to the high tertiary carbon content, which are prone to scission; 2) the characteristics of the crosslinking process in the post-gel region where high molecular weight chains are preferentially incorporated to the gel fraction.

Since every single carbon atom of the copolymer chains has the same probability of being affected by the radiation process, those molecules of the soluble fraction with higher mass have a higher probability to be involved in the crosslinking process and, therefore, they will be preferentially attached to the gel fraction. As a result of this process, at higher doses of radiation, the sol fraction is enriched in its composition by small chains that were produced by scission along the whole radiation procedure.

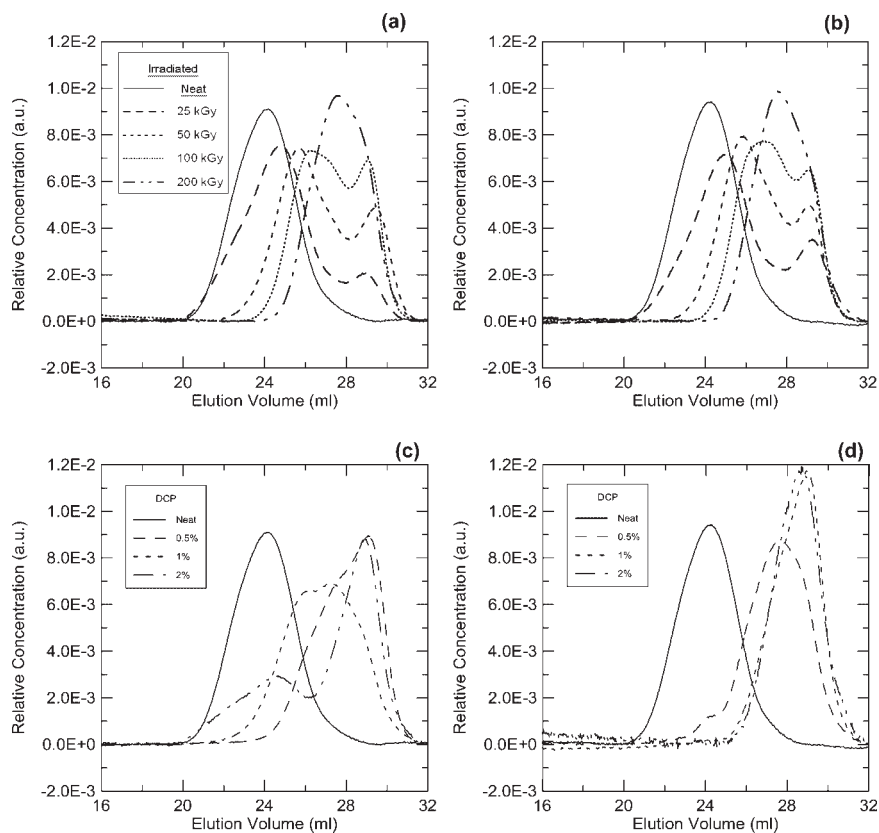


Figure 2. Molecular weight distributions by SEC of β -irradiated terpolymers: (a) EPDM-1; (b) EPDM-2 and DCP crosslinked terpolymers: (c) EPDM-1; (d) EPDM-2.

The values of the gel content are displayed in Figure 3. The elevated values of gel content obtained show that the efficiency in the crosslinking process is very high. This is attributable to the high content of unsaturations of both EPDMs. Even at low irradiation doses (25 kGy) the gel content is greater than 80%. We observe that EPDM-2 possesses higher gel contents than EPDM-1 on the whole irradiation range. This means that EPDM-1 needs higher irradiation doses to reach a determinate gel content. The difference in behavior of both copolymers is a consequence of the higher diene content in EPDM-2, which makes it more sensible to use β radiation.

Due to the high effectiveness of the crosslinking reaction, even at low irradiation doses we have no experimental data of the pre-gel region. But we can infer from the presented results that at low irradiation doses there is a considerable amount of chain scission reactions, which involve preferentially tertiary carbons in EPDM terpolymers. The molecular structure of EPDM terpolymers with high propylene content is responsible for this behavior. The chain scission rate should diminish at higher irradiation doses, as the concentration of tertiary carbons decreases.

Figure 2 also shows the MWD determined by SEC of the soluble fraction from DCP crosslinked samples extracted by xylene. The doses of DCP that were used in this work provided crosslinked samples in the post-gel region with

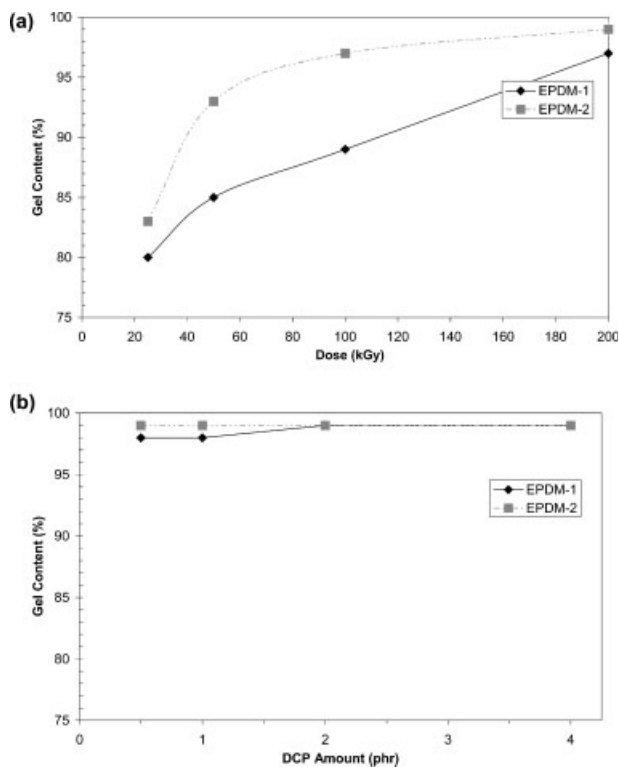


Figure 3. Gel content versus a) β -irradiation dose and b) DCP amount.

high gel content. As the gel fractions obtained in this case were very high, the soluble fraction of several samples (2 and 4 phr DCP) was not enough to be injected in the chromatograph and we had here more difficulties to run the SEC experiments. We attribute these problems to the inconsistency observed in Figure 2c, where the evolution of the SEC curves for 0.5 and 1% was not in accordance with our expectations. Nevertheless, the comparison of the results obtained from the crosslinked samples with those of the original terpolymers, shows again a very important reduction in molecular weight (\bar{M}_w , \bar{M}_n) with respect to those of the virgin materials. This type of evolution is comparable with the results observed with the irradiated samples.

These results confirm that considerable quantities of chain scission reactions are taking place. As the amounts of DCP are increased, the low molecular weight peak increases its intensity, leading to a bimodal distribution in the case of EPDM-1. Whereas for EPDM-2, with higher diene content, this fact is not so evident, probably because its higher diene content increases the efficiency of the linking process of higher molecular weight chains to the gel fraction.

FTIR Characterization

The decrease in intensity of the ENB dienic double bond characteristic band at 808 cm^{-1} [20,21] was followed during the crosslinking process. The $(\text{CH}_2)_n$ ($n \geq 4$) rocking band at 721 cm^{-1} , which is not affected by crosslinking was used as an internal standard. [22,23] Figure 4 displays the results of FTIR analysis of β -radiation and DCP crosslinked samples. The decrease in the double bond from the ENB monomer is more important at low irradiation doses (50 kGy) and low DCP amounts (<2 phr). At higher irradiation doses/DCP amounts, the decrease is reduced considerably, leading to an almost constant value. The decrease in β -radiation crosslinked terpolymers is slightly higher than in DCP crosslinked samples.

Additionally, one of the degradation processes related to carbonyl oxidation was also monitored. The contributions of carbonyl groups (aldehydes, ketones and acids) were collected between the range of 1705 and 1750 cm^{-1} , and are also shown under the symbol (C=O). They prove that products with a lower degree of oxidation are obtained with β -radiation. [9–11] In fact, in the case of β -irradiated terpolymers the oxidative degradation is very low, because no appreciable changes in the magnitude of the C=O peaks can be observed. In contrast, in the case of DCP crosslinked samples, the increase in degradative oxidation is progressive when increasing DCP amounts.

Rheological Characterization

Figure 5 shows the evolution of the elastic modulus with frequency for the irradiated and DCP crosslinked terpolymers at 90°C . The range of frequencies studied covers

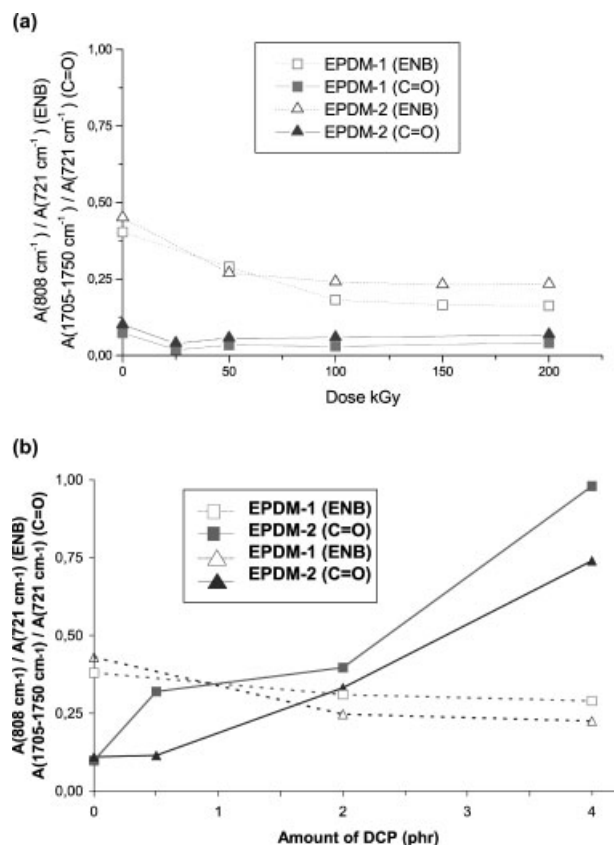


Figure 4. FTIR analysis of (a) β -irradiated and (b) DCP crosslinked samples.

the transition region between the terminal zone and the rubbery plateau of the original terpolymers. The decay of the modulus in the terminal zone is severely restricted by the irradiation process. At low irradiation doses (25–50 kGy) the gel has a low crosslinking density and, therefore, the values of $G'(\omega)$ are still dependent on the oscillatory frequency imposed to the polymer. At low frequencies (<1 rad/s) the values of $G'(\omega)$ involve mostly the effect of the contribution of active elastic chains induced by permanent crosslinking, whereas at higher frequencies they add the contribution of physical entanglements which cannot relax in the oscillatory period of time imposed to the sample. The lower the radiation dose, the higher the slope of the G' vs. ω curves.

The evolution of the magnitude of the observed elastic modulus $G'(\omega)$ in shear shows the same tendency for both EPDM terpolymers. At low irradiation doses (25 kGy) there is a dramatic decrease in the G' values with respect to those of the original terpolymer. At higher irradiation doses (100 kGy and 200 kGy) this tendency is reverted and the G' values begin to grow with the radiation dose. This behavior may be attributed to the high scission rate caused by the elevated concentration of tertiary carbons due to the presence of the propylene units in the main chain of the original terpolymers. At low irradiation doses it causes a noticeable decrease in the $G'(\omega)$ data in comparison with the values for

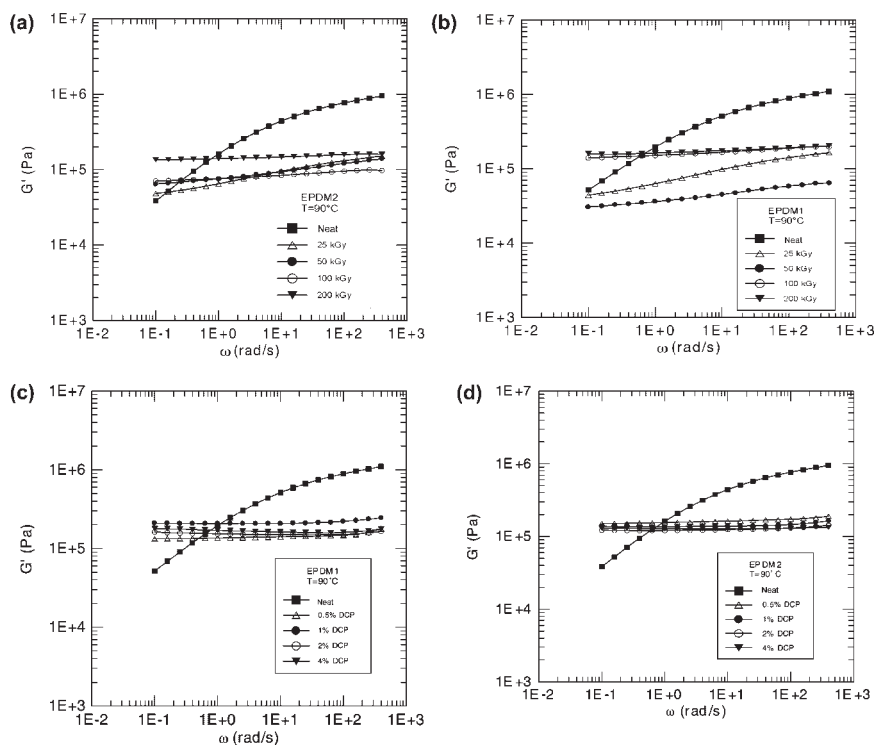


Figure 5. Storage modulus (G') versus frequency for β -irradiated samples: (a) EPDM-1; (b) EPDM-2 and DCP crosslinked samples; (c) EPDM-1; (d) EPDM-2.

the original terpolymers. As the irradiation doses are raised, the concentration of tertiary carbons is reduced and the dominant role of the crosslinking reactions causes a gradual increment in the values of $G'(\omega)$ that ends up at the typical elastomeric plateau values of $G'(\omega)$. The intensity of the decay of G' for EPDM-1 and EPDM-2 at low levels of radiation is consistent with the measured values of p_0/q_0 , which indicate that EPDM-1 has a much higher ratio of scission to crosslinking than EPDM-2.

The values of the loss tangent, $\tan \delta (=G''(\omega)/G'(\omega))$, for the crosslinked samples were also determined. Figure 6 shows this property for the irradiated and DCP crosslinked EPDMs as a function of the oscillatory frequency at 90 °C. In the range of frequencies chosen the relaxation associated to the terminal zone is very intense for original EPDM terpolymers. The intensity of the relaxation falls down when the irradiation doses are increased. At high irradiation doses the relaxation disappears as a consequence of the formation of new crosslinks between chains that inhibit the chain flow. The main energy dissipation factor is due to intermolecular friction between chains. Therefore, as the degree of crosslinking increases the elastic behavior is increased. These results are in good agreement with the shear modulus $G'(\omega)$.

As shown in Figure 5, the higher levels of crosslinking achieved with the peroxide treatment give almost frequency independent G' behavior at all concentrations of DCP. Again

the values of $G'(\omega)$ at the higher frequencies are lower than the corresponding values for the original terpolymers. No significant changes in values of the plateau modulus with the concentration of DCP were observed. This could be attributed to higher levels of crosslinking obtained with the chemical process. The relaxation in $\tan \delta$, associated to the terminal region disappears again for all DCP crosslinked samples. Due to the high levels of crosslinking and scission achieved in these samples the $G'(\omega)$ and $\tan \delta$ values obtained with different amounts of DCP do not differ significantly.

Table 2 presents additional results obtained in an Oscillating Disc Rheometer. In order to study the effect of the amount of DCP and the temperature of the reaction on the curing curves, two different amounts of DCP (2 and 4%) were used. Higher amounts of DCP accelerate the beginning of the reaction, expressed as the scorch time, t_{s2} , and also reduce the time to reach 50% and 90% cure, t_{c50} and t_{c90} , respectively. Besides, higher diene wt.-% of the EPDM-2 terpolymer speeds up the crosslinking reaction in comparison to EPDM-1.

DSC Characterization

Crosslinking reduces molecular mobility, and this is regained only by appropriate thermal activation at higher temperatures through an increase in the glass transition

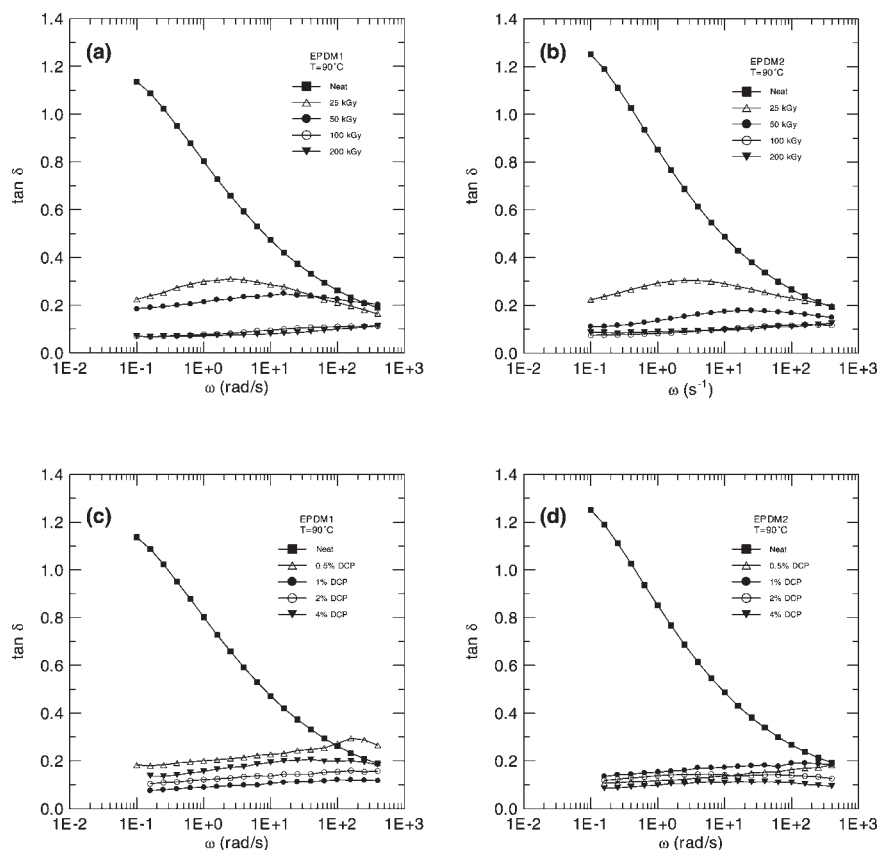


Figure 6. Loss tangent ($\tan \delta$) versus frequency for β -irradiated samples: (a) EPDM-1; (b) EPDM-2 and DCP crosslinked samples: (c) EPDM-1; (d) EPDM-2.

temperatures (T_g). There is a parallel decrease in the magnitude of the ΔC_p step that vanishes for heavily crosslinked materials.^[24] Table 3 shows the thermal properties of EPDM-1 and EPDM-2 before and after crosslinking. In the case of the β -irradiated samples, no significant changes were observed in the T_g values, however, ΔC_p , which is a more sensible parameter,^[24,25] shows a slight decrease with crosslinking. The values of T_g for EPDM-1 at DCP show a declining tendency in opposition to what is expected for a pure crosslinking process. This behavior may be attributable to the higher degrees of chain scission detected in this polymer. Low molecular weight chains produced by scission

or increasing amounts of networks defects could have a plastizing effect reducing the value of T_g .

Mechanical Properties

Table 4 shows the tensile properties of peroxide and β -radiation crosslinked EPDMs. β -Radiation crosslinked samples at 25 kGy and 50 kGy show a very good balance between tensile strength and elongation at break. There is a simultaneous increase in both tensile strength and elongation at break at low irradiation doses. These results are better than those obtained from the peroxide

Table 2. Vulcanization data from oscillant disc rheometer.

	2 phr DCP amount				4 phr DCP amount	
	EPDM-1		EPDM-2		EPDM-1	EPDM-2
	155 °C	190 °C	155 °C	190 °C	190 °C	190 °C
t_{S_2S}	81	33	63	31	28	26
$t_{C_{50S}}$	522	121	432	112	108	108
$t_{C_{90S}}$	1489	236	1233	204	242	224
$M_L \text{ N} \cdot \text{m}$	2.55	2.55	2.55	2.65	2.65	2.75
$M_H \text{ N} \cdot \text{m}$	9.12	9.09	8.43	8.53	12.55	11.96
$(M_H - M_L) \text{ N} \cdot \text{m}$	6.57	6.54	5.88	5.88	9.90	9.21

Table 3. Thermal properties.

Material	DCP amount	T_g	ΔC_p	Irradiation dose	T_g	ΔC_p
	phr	°C	J/(g·°C)		kGy	°C
EPDM-1	0.0	-46.2	0.67	–	–	–
	0.5	-46.1	0.64	25	-45.5	0.64
	1.0	-45.9	0.63	–	–	–
	2.0	-42.6	0.61	–	–	–
	4.0	-41.8	0.61	200	-46.6	0.63
EPDM-2	0.0	-44.1	0.69	–	–	–
	0.5	-43.4	0.63	25	-43.9	0.66
	1.0	-43.0	0.62	–	–	–
	2.0	-45.7	0.62	–	–	–
	4.0	-44.7	0.61	200	-43.5	0.63

crosslinked samples in the range of concentrations covered in this work.

The tensile strength and the elongation at break at higher irradiation doses (100–200 kGy) decrease due to a combination of crosslinking and scission reactions, as observed before.

The compression set test is a very easy and useful tool when developing a new formulation for a crosslinked compound. The results are shown in Table 5. The minimum compression set corresponds to a DCP amount of 4 phr in both EPDMs. Higher amounts of DCP were used, but the samples were rejected because they were too fragile and broke during the test. The results in the test at room temperature for 72 h display that DCP crosslinked samples with an amount of 0.5 phr are similar to β -radiation crosslinked samples with a dose of 200 kGy.

However, in the test carried out at 150 °C for 72 h, the increase in compression set is much more dramatic for DCP crosslinked samples. It can be attributed to the lower rate of degradation typical of β -radiation crosslinking processes. Table 5 also shows values of Shore A hardness. The β -radiation irradiated samples provide lower values of hardness, when compared to DCP crosslinked samples. The

dose of 200 kGy is equivalent to the amount of 0.5–1 phr of DCP. An enhancement in the state of cure can be achieved with higher β -irradiation doses or the same doses in combination with coagents of cure.

The values of Shore A hardness are also reported in Table 5. They rise with the addition of increasing amounts of DCP and with increasing irradiation doses, although the increase is more intense in the case of DCP crosslinked samples. The values of irradiated at 200 kGy coincide with the values at 0.5 phr DCP, indicating that they have a similar state of cure. At very high DCP additions the values of Shore A hardness increase in a lesser grade, indicating the presence of degradation reactions.

Conclusion

The structure of both ethylene-propylene-diene terpolymers with high propylene and diene content determines their response to the crosslinking process. It has been verified that their very high tertiary carbon content, results in an important amount of chain scission reactions, reducing significantly the efficiency of the crosslinking process, either by dicumyl peroxide or β -radiation. The rheological measurements suggest that the chain scission processes are more important during the first steps of the reaction – either by radiation or peroxide treatment – and diminish at higher irradiation doses, as the concentration of tertiary carbons decreases. On the other hand, the presence of unsaturations favors a fast curing rate compensating in part the consequences of the high scission levels and allowing to reach the gelation point at reasonable levels of radiation doses or peroxide concentration.

In the range of doses and concentrations explored in this work, β -radiation crosslinked EPDMs provide better tensile properties and have a good performance at high temperatures without big losses in their storage modulus. An enhancement in the state of cure can be achieved with higher radiation doses. The process of crosslinking, either by β -radiation or peroxides has been monitored by FTIR, stating

Table 4. Tensile properties.

Amount of DCP phr	Irradiation Dose kGy	Tensile strength		Elongation at break	
		MPa		%	
		EPDM-1	EPDM-2	EPDM-1	EPDM-2
0		0.56 ± 0.01	0.55 ± 0.04	218 ± 4	221 ± 13
0.5		1.24 ± 0.05	1.05 ± 0.08	252 ± 17	175 ± 36
1		1.10 ± 0.08	1.04 ± 0.14	124 ± 10	114 ± 27
2		1.04 ± 0.08	1.02 ± 0.06	86 ± 8	92 ± 7
4		0.81 ± 0.03	0.79 ± 0.05	48 ± 2	49 ± 3
	25	1.32 ± 0.01	1.62 ± 0.28	>1660	>1660
	50	2.26 ± 0.23	1.09 ± 0.08	965 ± 71	423 ± 63
	100	1.25 ± 0.11	1.17 ± 0.10	321 ± 48	252 ± 42
	200	1.08 ± 0.07	1.17 ± 0.03	153 ± 16	147 ± 10

Table 5. Compression set and Hardness Shore A.

Amount of DCP phr	Irradiation Dose kGy	Compression set				Hardness Shore A	
		Room temp., 72 h		150 °C, 72 h		EPDM-1	EPDM-2
		EPDM-1	EPDM-2	EPDM-1	EPDM-2		
0		–	–	–	–	40	39
0.5		8	8	23	22	46	45
1		3	3	11	10	49	48
2		1	1	7	8	52	51
4		1	1	5	5	57	56
6		Fragile	Fragile	Fragile	Fragile	57	56
10		Fragile	Fragile	Fragile	Fragile	58	57
	25	29	28	63	70	43	42
	50	23	18	50	51	44	45
	100	15	11	32	26	45	46
	200	8	8	16	14	46	47

that lower oxidative degradation and better crosslinking efficiency have been obtained for the β -irradiated terpolymers. In terms of other mechanical properties, such as hardness Shore A and compression set, more rigid samples were obtained with peroxides.

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