

Correlations between the Processing Variables and Morphology of Crosslinked Polyethylene

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ABSTRACT: Crosslinked polyethylene (XLPE) is progressively replacing other types of polyethylene in electric cable insulation because of its combination of better mechanical and thermal performance and good dielectric properties. Besides its influence on the mechanical and thermal properties, the morphology plays a very important role in the electrical behavior of XLPE. The morphology has been studied in terms of the crystallinity and crosslinking density. These two apparently independent parameters govern the morphology of XLPE and have been investigated in connection with the systematic variation of the processing param-

eters (crosslinker concentration, cure time, and temperature). The materials have been characterized in terms of the extent of crosslinking (the gel content), the crosslinking density (the average molecular weight between crosslinks), and the crystallinity. A morphological model is proposed for these materials in terms of the mechanisms and rates of the processes involved. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 222–230, 2004

Key words: crosslinking; morphology; polyethylene (PE); processing

INTRODUCTION

Crosslinked polyethylene (XLPE) combines the good dielectric properties of other types of polyethylene with improved mechanical and thermal behavior. Most importantly, it retains adequate mechanical properties at temperatures at which low-density polyethylene (LDPE) becomes too soft. This set of characteristics has been responsible for the progressive replacement of low- and high-density polyethylenes in electric cables by XLPE.^{1–3} The most employed crosslinking processes are based on chemical reactions, such as the thermally activated decomposition of peroxy compounds, the grafting of silane compounds onto chains, and the irradiation of LDPE with a high-energy electron beam.^{3,4} In the first method, dicumyl peroxide (DCP) is the most extensively used radical source; in the second method, vinyltriethoxysilane or vinyltrimethoxysilane is grafted onto chains, with small quantities of peroxides used as radical initiators, and this is followed by silane hydrolysis and silanol condensation.^{5–12} The silanol groups condense,

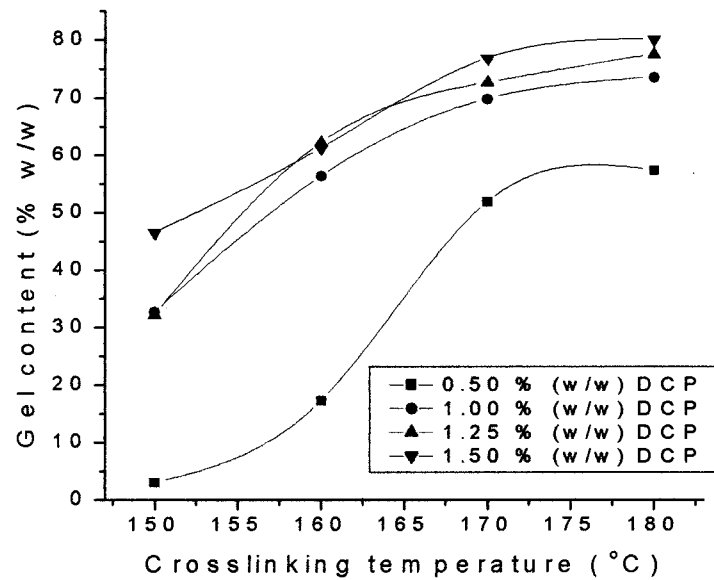
with the loss of water, thus interconnecting polymer chains. It is a common practice to accelerate this reaction with the addition of catalytic amounts of organotin compounds such as dibutyl tin dilaurate.^{5,9,12} In the irradiation process, the crosslinking degree is limited by the depth reached by the electron beam, and in the silane grafting process, the permeation of water into the bulk of the polymer to promote the hydrolysis of the alkoxy silanes is the rate-determining step of the process. In both cases, the final material has a crosslinking density gradient along its thickness. The use of peroxides promotes a more uniform distribu-

TABLE I
Parameters Used in M_c Calculations
from the Swelling Data

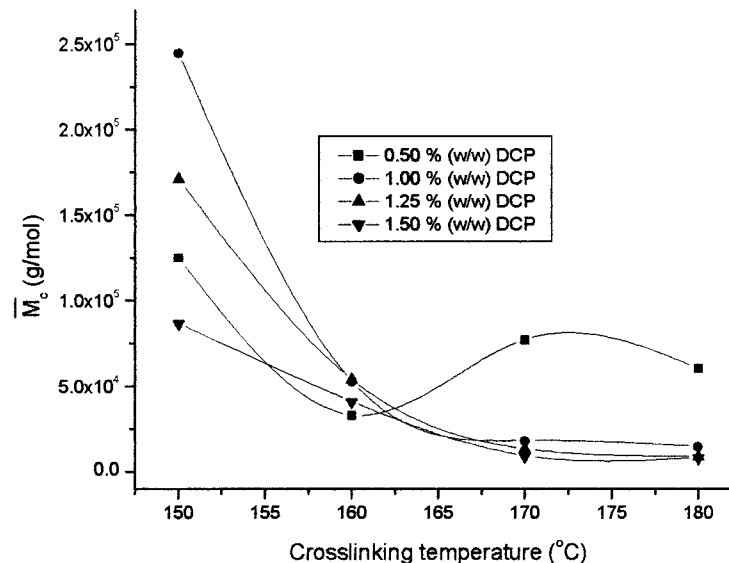
Parameter	Data
M_{solv}	138.25 g
ρ_{solv}	0.88 g/cm ³
V_1	157.1023 cm ³
R	1.987 cal/K mol
Temperature	298 K
	463 K
δ_1	8.80 (cal/cm ³) ^{1/2} a
δ_2	8.79 (cal/cm ³) ^{1/2} a
χ	0.34 (298 K)
	0.01 (463 K) ^a
ρ	0.927 g/cm ³ (298 K)
	0.7536 g/cm ³ (463 K) ^b

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(A)



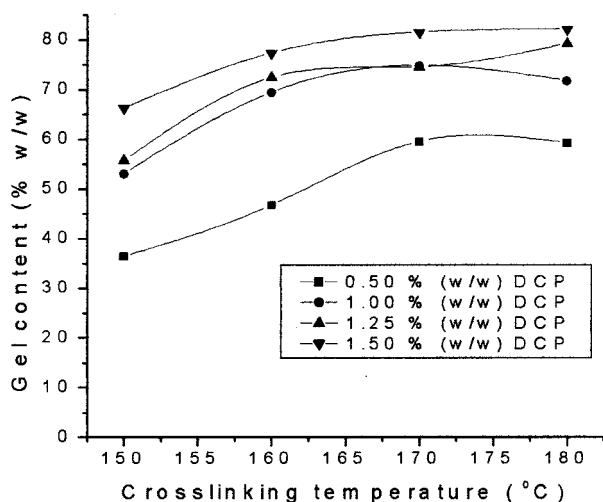
(B)

Figure 1 Dependence of (A) the gel content and (B) M_c on the crosslinking temperature (cure time = 5 min).

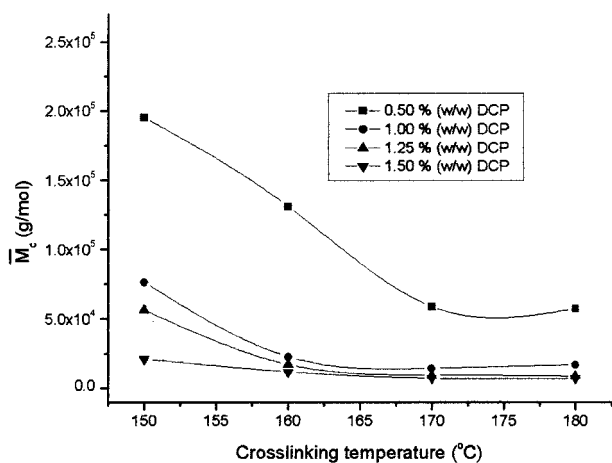
tion of chain interconnections all over the bulk material. On the other hand, the byproducts generated during peroxide decomposition, such as acetophenone, α -methylstyrene, and cumyl alcohol, can exert a deleterious effect on the electrical performance of XLPE, even in very small quantities, notably under AC conditions.¹³⁻¹⁷

Besides the influence exerted on the mechanical and thermal properties, the morphology plays a very important role in the electrical behavior of XLPE, including the water treeing resistance: polymer-insulated

cables are laid in an underground environment, and water from the soil can slowly diffuse through the protective layers of the cable, forming treelike structures, which actually are water-filled microcavities (ca. 1 μm or less).¹⁻³ Water treeing is the main cause of insulation breakdown in medium-voltage cables, and the first approach for assessing the influence of the morphology on this phenomenon should obviously be a detailed morphological description of the polymer.^{3,18-20} Small modifications in the processing conditions can induce strong effects on the polymer prop-



(A)



(B)

Figure 2 Dependence of (A) the gel content and (B) M_c on the crosslinking temperature (cure time = 10 min).

erties, but a systematic study of the correlations of processing parameters with the morphology cannot be found in the literature to our knowledge.

We have studied the peroxide crosslinking process in XLPE production, and this article describes the correlations between the processing variables for XLPE manufacturing (the crosslinker concentration, thermal pressing time, and temperature) and the resulting structural parameters (the crosslinking density, gel content, average chain length between interconnecting points, and crystallinity).

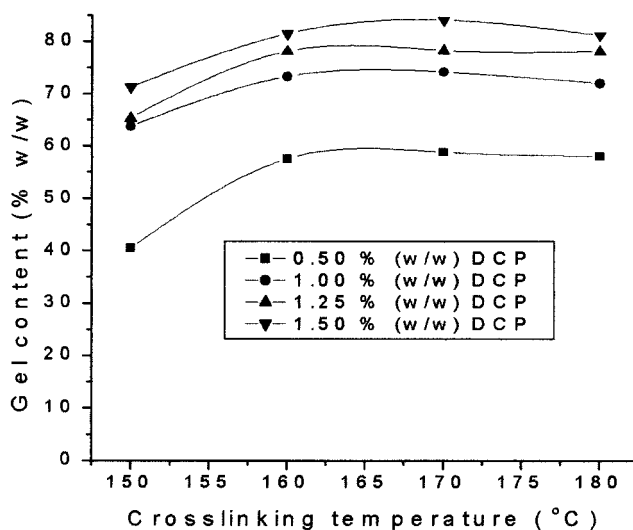
EXPERIMENTAL

Materials

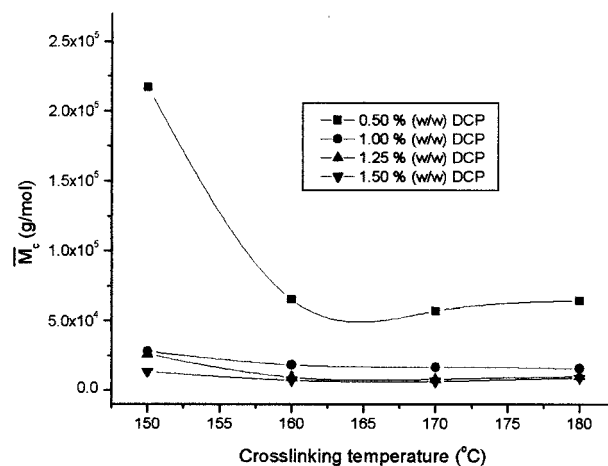
The starting LDPE was kindly supplied by OPP (Poliétilenos S.A. Brazil) and had the following initial

characteristics: weight-average molecular weight = 135,000, number-average molecular weight = 15,000, density = 0.921 g/cm^3 , and melt index = 3.8 g/10 min.

LDPE in a powder form, containing the required amount of DCP (0.50, 1.00, 1.25, or 1.50% w/w), previously milled and sieved, was thermopressed in a Shulz model PHS 15 press. Samples in disk form (diameter = 11 cm and thickness of 0.1 cm) were separated from aluminum molds by cellulose acetate sheets. The thermal pressing was performed under a load of 4 tons for 5, 10, 15, or 20 min at 150, 160, 170, or 180°C.

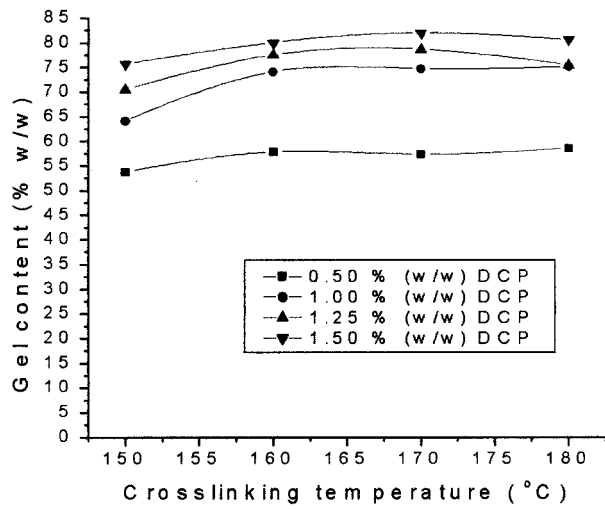


(A)

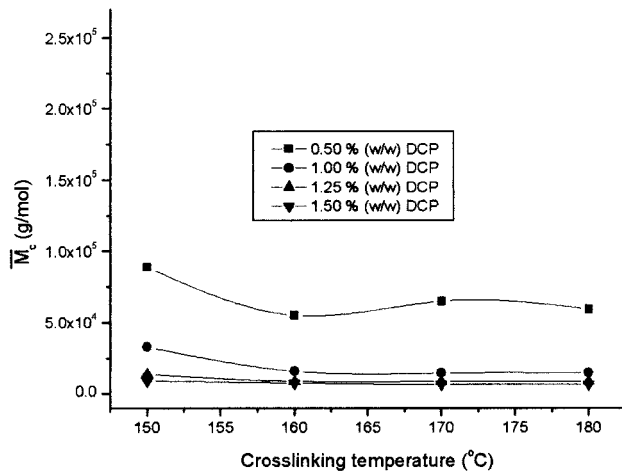


(B)

Figure 3 Dependence of (A) the gel content and (B) M_c on the crosslinking temperature (cure time = 15 min).



(A)



(B)

Figure 4 Dependence of (A) the gel content and (B) M_c on the crosslinking temperature (cure time = 20 min).

X-ray diffractometry: wide-angle X-ray scattering (WAXS)

The WAXS spectra were made with Co $K\alpha$ radiation ($\lambda = 1.79026 \text{ \AA}$) in a Phillips X'Pert conventional horizontal-axis instrument at a scanning rate of $1^\circ/\text{min}$ between $2\theta = 3^\circ$ and $2\theta = 60^\circ$. The crystallinity was calculated by fitting into three Gaussian curves with software with the following relationship:

$$\text{Crystallinity (\%)} = \frac{\text{Area 2} + \text{Area 3}}{\text{Area 1} + \text{Area 2} + \text{Area 3}} \times 100 \quad (1)$$

where area 1 corresponds to the amorphous halo and areas 2 and 3 correspond the crystalline peaks at $2\theta = 21.22^\circ$ and $2\theta = 23.63^\circ$, respectively.

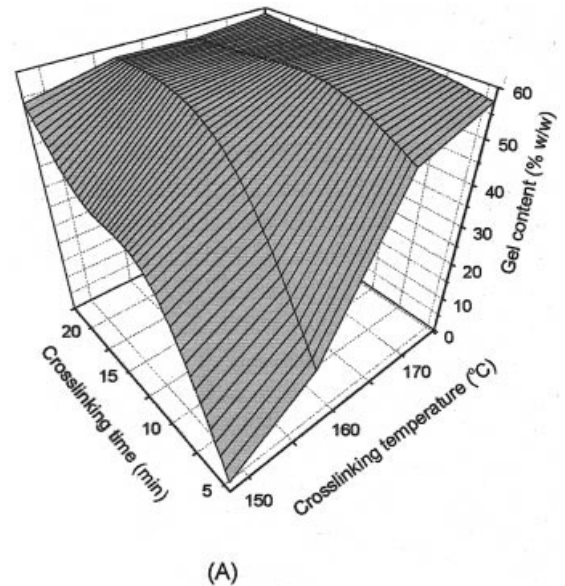
XLPE characterization

Gel content

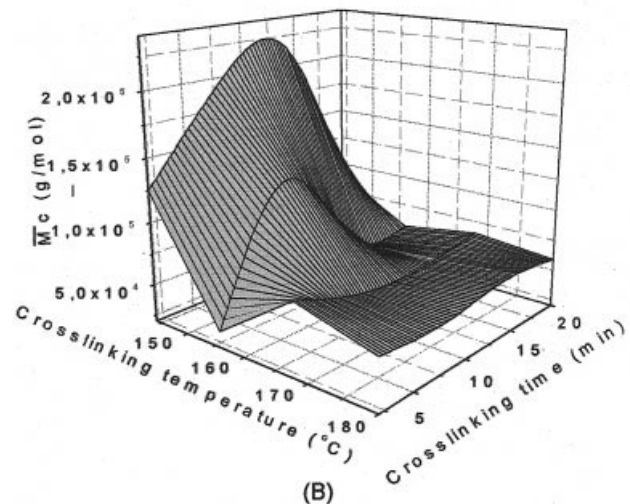
Gel content determinations were performed with decaline (Vetec P.A.) as a solvent under reflux (190°C) for 6 h. Samples of about 0.1 g were placed in a 100-mL, round-bottom flask containing 20 mL of the solvent and connected to a reflux condenser. After drying to a constant weight (ca. 16 h) at 70°C , the extracted samples were reweighed, and the fraction of the crosslinked material was calculated from the initial and final masses.

Average molecular weight between crosslinks (M_c)

Swelling at room temperature. After extraction, as previously described, the weighed samples were im-

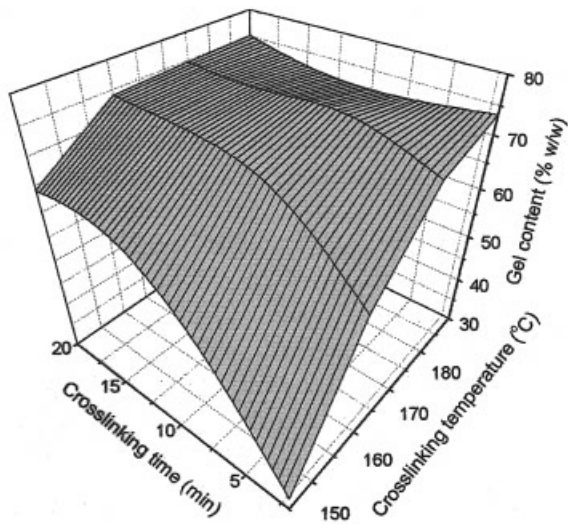


(A)

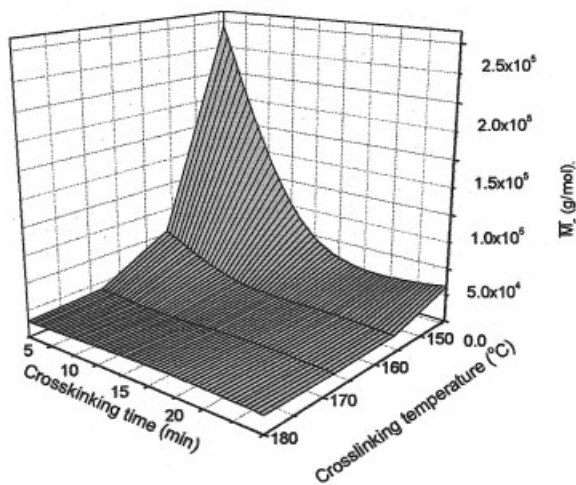


(B)

Figure 5 Correlation of the time, temperature, and (A) gel content or (B) M_c , with 0.50% DCP.



(A)



(B)

Figure 6 Correlation of (A) the gel content and (B) M_c with the time and temperature of thermal pressing, with 1.00% DCP.

mersed in 30 mL of decaline. The flasks were stirred for 24 h and kept in the dark for 2 months at room temperature. Afterwards, the samples were reweighed to calculate the amount of the absorbed solvent.

Hot swelling. Immediately after extraction, the hot samples were rapidly filtered to remove the soluble fraction, weighed, and dried to a constant weight (ca. 16 h). The dried samples were reweighed, and M_c was calculated from the mass difference between the swollen and dried samples.

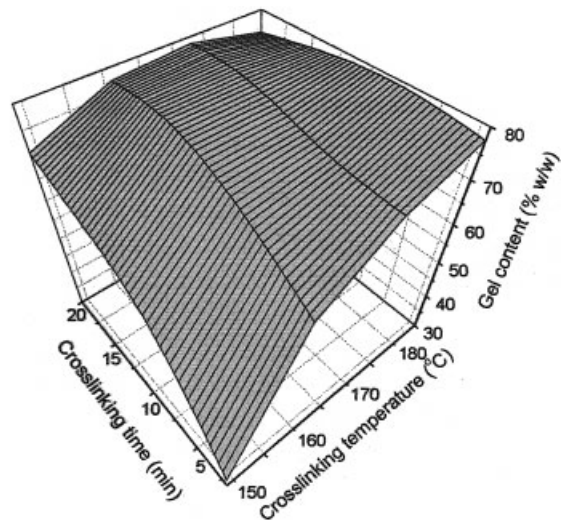
Density

The density determinations were performed according to ASTM D 792/91²¹ with a Sartorius BP210S

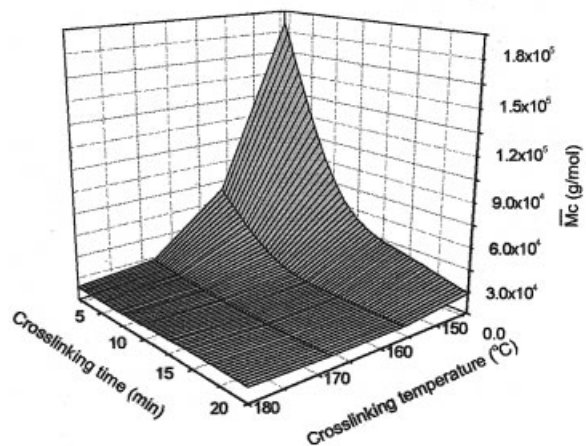
analytical balance with a YDK01 specific accessory. As a liquid medium, isopropyl alcohol (99.5%; P.A. Nuclear) was used with a density of 0.78336 g/cm³ at 22°C.

RESULTS AND DISCUSSION

In peroxide processes, the crosslinker concentration, cure time, and temperature are the main variables determining the extent and density of crosslinking and, consequently, the resulting morphology. The extent of crosslinking (the gel content) expresses the mass of chains that are effectively interconnected and is determined by the measurement of the fraction of material not extractable by the solvent. In industrially



(A)



(B)

Figure 7 Correlation of (A) the gel content and (B) M_c with the time and temperature of thermal pressing, with 1.25% DCP.

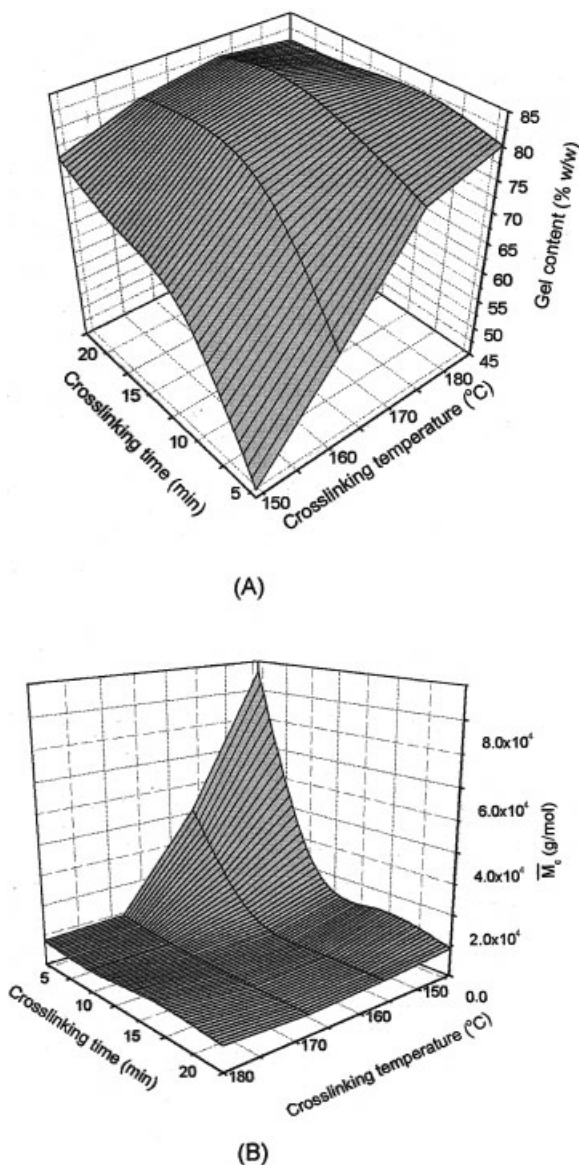


Figure 8 Correlation of (A) the gel content and (B) M_c with the time and temperature of thermal pressing, with 1.50% DCP.

manufactured XLPE, the gel content is 60–85%. Previous work⁵ has shown that the gel content levels off for DCP concentrations greater than 2%. Having in mind that byproducts of DCP are deleterious for electrical performance, we have restricted the peroxide concentration to 0.50–1.50% (w/w). The classical method of determining the network crosslinking density is based on the Flory–Rehner theory^{22–24} of swelling at equilibrium, in which M_c is determined with eq. (2). This method has been extensively applied to vulcanized rubbers,^{25–27} but for XLPE, few references can be found:^{5,28–30}

$$\nu = \rho/M_c = -[\ln(1 - V_r) + V_r + \chi V_r^2] / \rho V_1 (V_r^{1/3} - V_r/2) \quad (2)$$

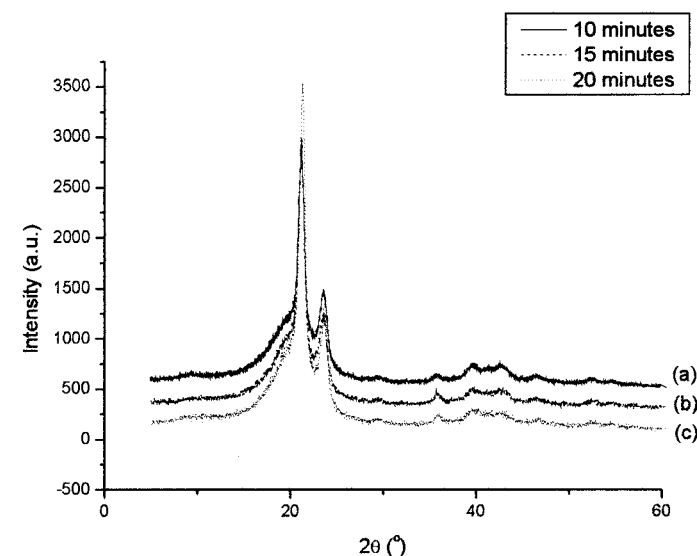
where ν is the crosslinking density or number of effective chains per volume, ρ is the polymer density, V_r is the reduced volume (the volume of the swollen sample/the volume of the dry sample), χ is the polymer–solvent interaction parameter, and V_1 is the molar volume of the solvent. The values used in the evaluation of the crosslinking density are listed in Table I.

Gel content

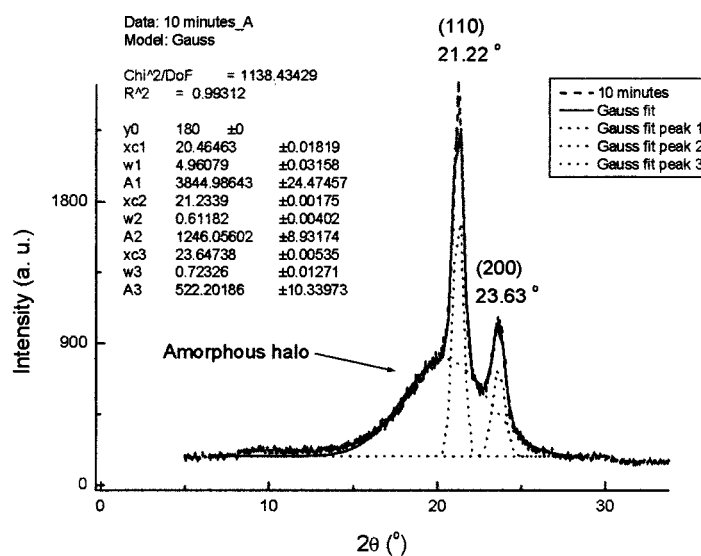
Figures 1(A)–4(A) depict the variations of the gel content as a function of the temperature for crosslinker concentrations of 0.50, 1.00, 1.25, and 1.50% with thermal pressing times of 5, 10, 15, and 20 min, respectively. The main conclusions drawn from these results are as follows. The maximum gel contents attainable for all times and temperatures are 59, 75, 79, and 84% for DCP concentrations of 0.50, 1.00, 1.25, and 1.50%, respectively. Beyond 15 min and 160°C, all the samples reached gel contents near their maximum limit, and so above this time and temperature, it is of no use to increase any of these variables, including the peroxide concentration. During the first 5 min at 180°C, a plateau is reached for the extent of crosslinking, for each DCP concentration, so no further time in the press is needed. In conclusion, any variation in the processing variables only makes a difference if variations in the peroxide concentration are tested below 160°C and 10 min. These results are well illustrated in the three-dimensional plots of Figures 5(A)–8(A), in which the surface tends to planarity from 10 min and 160°C for all peroxide concentrations. Considering the half-life of DCP (14 min at 150°C),³² we find that the lower crosslinking densities are due to the lowering of the radical concentration. Thus, for commercially acceptable XLPE, the DCP concentration has to be set above 1.0% for any cure conditions.

M_c

Figures 1(B)–4(B) describe the variations of the average molecular weight between interconnection points for crosslinker concentrations of 0.50, 1.00, 1.25, and 1.50% and for residence times of 5, 10, 15, and 20 min, respectively. The high initial values of M_c are due to the vinyl coupling of chain ends, which are more reactive sites than tertiary carbon atoms.²⁹ As with the gel content discussed previously, we can summarize the main results as follows. The minimum values attainable for M_c are 57,000, 14,000, 8000, and 6400 g/mol for DCP concentrations of 0.50, 1.00, 1.25, and 1.50%, respectively. The major part of the crosslinking process occurs during the first 5 min of the reaction. The reduction of M_c in this interval depends on the temperature. For example, at 150°C, it drops 240,000 to 76,000 g/mol for samples containing 1.00% DCP. For



(A)



(B)

Figure 9 (A) X-ray diffraction patterns for completely crosslinked XLPE (extracted samples) with cure times of (a) 10, (b) 15, and (c) 20 min (0.5% DCP and 150°C) and (B) Gaussian fitting of the crystalline peaks and the amorphous halo.

higher temperatures, the drop is not as drastic (e.g., from 53,000 to 22,600 g/mol at 160°C with the same peroxide concentration). This is due to the larger number of free radicals formed at higher temperatures, which lead to lower M_c 's. Just as for the gel content, a plateau is reached for M_c after 10 min at temperatures of 160°C and higher, even with the use of greater concentrations of the crosslinker. This effect is clearly evident in the 3D plots of Figures 5(B)–8(B).

The results indicate that the gel content and M_c are directly correlated. For example, gel contents of 82–84, 77, 70, and 55% correspond to M_c values of 6400, 9000,

17,000–14,000 g/mol, and 55,000–60,000 g/mol. This means that the possibility of the same gel content being associated with different M_c 's is ruled out. It has been verified that no drop in M_c occurs at higher temperatures and longer times under the conditions employed.

The results obtained from swelling tests run at room temperature represent the behavior of the amorphous phase only because the solvent cannot easily penetrate the crystalline regions. The samples used were extracted ones, and the mass values were corrected with WAXS data to consider only the amorphous mass in

the M_c calculations. The entirely crosslinked phase has a crystallinity of about 32%, and this shows that the crosslinking process brings about a reduction of around 12%, in comparison with that of the original LDPE (44%). The corresponding diffraction patterns are shown in Figure 9.

The values of M_c in swelling tests run at room temperature are much lower than those in tests run under hot conditions. Typically, M_c 's of approximately 190 g/mol for samples crosslinked with 1.0% DCP for 5 min have been found. This result leads us to the following question: because the crystallites cannot accommodate the crosslinks, how do the two simultaneous and apparently independent processes (crosslinking and crystallization) interfere with each other? One hypothesis considers that before the crosslinking, the sample is completely molten, amorphous, and homogeneous. The crystallization begins only after the network formation, and the crosslinks stay outside the crystallites. Under these conditions, M_c should be the same, whether measured at room temperature or in the molten state. Another hypothesis is that even in the molten state, because of the high viscosity of the mass, some ordered regions remain in the melt and act as nucleating agents for heterogeneous crystallization. These regions are not accessible to the free radicals. Moreover, the viscosity begins to increase dramatically with incipient crosslinking, even before the maximum concentration of radicals is reached at 150°C, and this makes it difficult to attain a homogeneous molten state.

The resulting situation is a bimodal distribution of crosslinks: long, linear chain lengths that participate in the crystallites and shorter ones confined to the amorphous phase. This model justifies the differences found for M_c 's determined at room temperature and in the molten state and a crystallinity of 32% even with high gel contents. Moreover, it justifies crystallization with very short M_c 's. In this context, the crystallization lamellar model proposed by Flory seems closer to reality than the chain-folded lamellar structure, as proposed by Hendra et al.²⁹

Altogether, the results obtained so far lead us to propose a morphological scheme for XLPE: crystalline regions interconnected via linear or crosslinked tie molecules embedded in an amorphous crosslinked matrix. Figure 10 illustrates these ideas.

CONCLUSIONS

The knowledge of the correlations between the processing conditions and resulting structure of XLPE is of primary importance for manipulating the variables involved. Depending on the time and temperature, the gel content and M_c can reach a plateau at which further increments in the peroxide concentration are detrimental because they only lead to more degradation

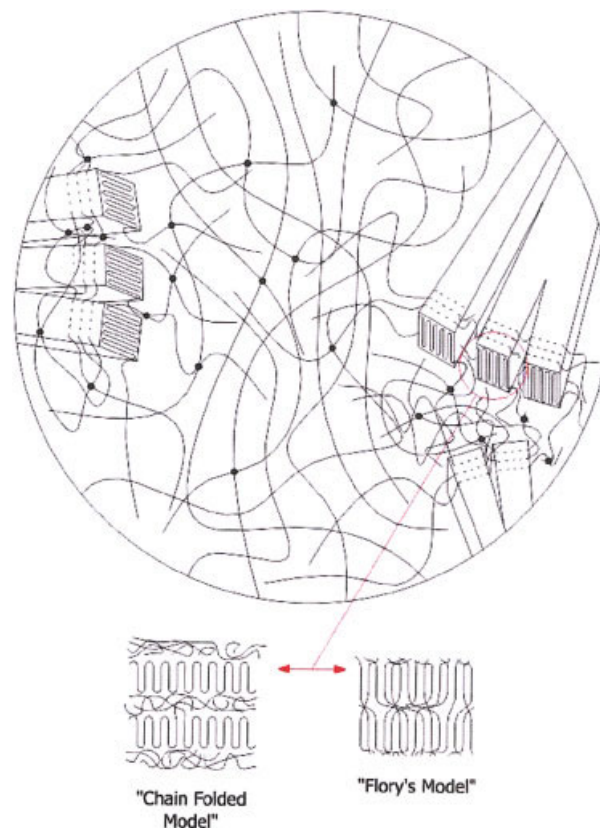


Figure 10 Sketch representing the proposed morphological model for XLPE.

products, without any effect on the structural parameters. The major part of the crosslinking process occurs during the first minutes of the cure, and so it is also of no use to extend the reaction for longer times. The crystallization mode is more like the Flory crystallization lamellar model than the chain-folded structure according to the differences found in the crosslinking densities for molten and crystalline samples.

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References

1. Steennis, E. F.; Kreuger, F. H. *IEEE Trans Electr Insul* 1990, 25, 989.
2. Ross, R. *KEMA Sci Tech Rep* 1990, 8, 209.
3. Ciuprina, F.; Teissèdre, G.; Filippini, J. C. *Polymer* 2001, 42, 7841.
4. Han, S. O.; Lee, D. W.; Han, O. H. *Polym Degrad Stab* 1999, 63, 237.
5. Celina, M.; George, G. A. *Polym Degrad Stab* 1995, 48, 297.
6. Beveridge, C.; Sabiston, A. *Mater Des* 1987, 8, 263.
7. Currat, C. *Wire J Int* 1984, 17, 60.
8. Kircher, K. *Chemical Reactions in Plastics Processing*, Hanser: Munich, 1987; p 153.
9. Lazar, M.; Rado, R.; Rychly, J. *Adv Polym Sci* 1990, 1, 149.
10. Gross, L. H. *Wire J Int* 1988, 21, 59.

11. Scott, H. G. (to Midland Silicones, Ltd.). U.S. Pat. 3,646,155 (1972).
12. Munteanu, D. In *Metal-Containing Polymeric Systems*; Sheats, J. E.; Carraher, C. E.; Pittman, C. U., Eds.; Plenum: New York, 1985; p 479.
13. Dissado, L. A.; Fothergill, J. C. In *Electrical Degradation and Breakdown in Polymers*; Stevens, G. C., Ed.; Peter Peregrinus: London, 1992.
14. Mitsumoto, S. I. *Annu Rep Conf Electr Insul Dielectr Phenom* 1996, 1, 157.
15. Ohki, Y.; Hirai, N.; Kobayashi, K.; Minami, R.; Okashita, M.; Maeno, T. *Annu Rep Conf Electr Insul Dielectr Phenom* 2000, 2, 535.
16. Amyot, N.; Lee, S. Y.; David, E.; Lee, I. H. *Annu Rep Conf Electr Insul Dielectr Phenom* 2000, 2, 743.
17. Das-Gupta, D. K.; Barbarez, M. K. *J Phys D: Appl Phys* 1973, 6, 867.
18. Chen, J. L.; Filippini, J. C. *IEEE Trans Electr Insul* 1993, 28, 271.
19. Raharimalala, V.; Poggi, Y.; Filippini, J. C. *IEEE Trans Dielectr Electr Insul* 1994, 1, 1094.
20. Fukuda, T.; Irie, S.; Asada, Y.; Maeda, M.; Nakagawa, H.; Yamada, N. *IEEE Trans Electr Insul* 1982, 17, 386.
21. *Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement*; ASTM D 792; American Society for Testing and Materials: Easton, PA, 1991.
22. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 11, 572.
23. Flory, P. J. *J Chem Phys* 1950, 18, 108.
24. Akcelrud, L. *Rev Bras Eng* 1993, 10, 107.
25. Amin, M.; Nasr, G. M.; Attia, G.; Gomaa, A. S. *Mater Lett* 1996, 28, 207.
26. Gwaily, S. E.; Badawy, M. M.; Hassan, H. H.; Madani, M. *Polym Test* 2003, 22, 3.
27. Youssef, M. H. *Polym Test* 2003, 22, 235.
28. Sawadzki, S. F.; Sereda, L.; Akcelrud, L. *Int J Polym Mater* 1996, 33, 31.
29. Hendra, P. J.; Peacock, A. J.; Willis, H. A. *Polymer* 1987, 28, 705.
30. Smedberg, A.; Hjertberg, T.; Gustafsson, B. *Polymer* 2003, 44, 3395.
31. *Polymer Handbook*, 3rd ed.; Brandrup, J.; Immergut, E. H., Eds.; John Wiley & Sons, Inc., New York: 1989; Vol. 10, p 15.
32. *Organic Peroxides*; Elf Atochem North America: Philadelphia, 1992.