Structural investigation of chemically crosslinked low density polyethylene

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The effects of chemical crosslinking on low density polyethylene are investigated, using electron microscopy, X-ray diffraction, n.m.r., and gel fraction determination. The results of these studies are discussed in terms of the degree of crosslinking estimated on the basis of peroxide content.

INTRODUCTION

This work is a continuation of our earlier work concerning the investigation of ultrasonic properties of this polymer[1,2]. The previous work done on this subject does not deal with the exact same polymer and does not cover the same field of interest[3]. As an example Charlesby[4] and Mandelkern[5] have investigated PE crosslinked by irradiation, whereas our interest is focused mainly on physical properties of chemically crosslinked low density PE.

Table 1 Gel fraction values in crosslinked polyethylene. Symbols: (1) refers to Di-Cup R; (2) refers to Luperox 130; (3) refers to Luperox 101; (0) refers to uncrosslinked PE; (a)–(e) refers to the peroxide concentration shown in column 2. In all other tables these symbols will be used

Number of sample	Peroxide concentration	Gel fraction (%)
1	2	3
1a	0.5	81.9
1b	1	82.1
1c	1.5	85.2
1d	2.0	87.0
1e	2.5	89.4
2a	0.5	64.0
2b	1	75.4
2c	1.5	83.3
2d	2.0	84.2
2e	2.5	86.5
3a	0.5	85.7
3b	1	86.5
3c	1.5	87.7
3d	2.0	89.2
3e	2.5	91.3

EXPERIMENTAL

Methods of preparation

The methods of preparation of XLPE used in this study have been described earlier[1,2,6]. For the experiments we used low density polyethylene Petrolen WJG-47 (this polymer is similar to I.C.I. product WJG-47) with a molecular weight of $\sim 32{,}000$ $\bar{M}_n$. The short chain branching according to ICI has been found to be Me/1000C = 30. The commercial and chemical names of the peroxides are 1-Di-Cup R, dicumyl peroxide, 2-Luperox 130, 2,5 dimethyl–2,5 bis-t-butyl-peroxy hesyne, and 3-Luperox 101, 2,5 dimethyl–2,5 bis-t-butyl-peroxy hexane. To accomplish the crosslinking process the weight % of the peroxides in polyethylene were (a), 0.5; (b) 1.0; (c) 1.5; (d), 2.0; (e), 2.5.

Gel fraction

Gel fraction was determined as the % fraction of the original weight of the sample after extracting for 4 h in boiling xylene followed by boiling in CH_3OH for 2 h and drying. The results are given in *Table 1.*

Density

Density measurements were performed by means of a gradient column. Results are given in *Table 2.* The degree of crystallinity was calculated using the following equation:

Table 2 Density and crystallinity of crosslinked polyethylene. Symbols as for *Table 1*

	Density (g cm^{-3})	Crystallinity (%)		Density (g cm^{-3})	Crystallinity (%)		Density (g cm^{-3})	Crystallinity (%)
1	2	3	4	5	6	7	8	9
1a	0.9165	43.7	2a	0.9155	43.0	3a	0.9150	43.7
1b	0.9153	42.9	2b	0.9150	42.7	3b	0.9144	42.2
1c	0.9150	42.7	2c	0.9145	42.3	3c	0.9140	42.0
1d	0.9141	42.0	2d	0.9130	41.3	3d	0.9145	41.6
1e	0.9133	41.5	2e	0.9120	40.6	3e	0.9125	41.1
0[a]	0.9141	42.0						

0[a] Values for uncrosslinked polyethylene

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Figure 1 **The surface of uncrosslinked PE (Magnification x6000)**

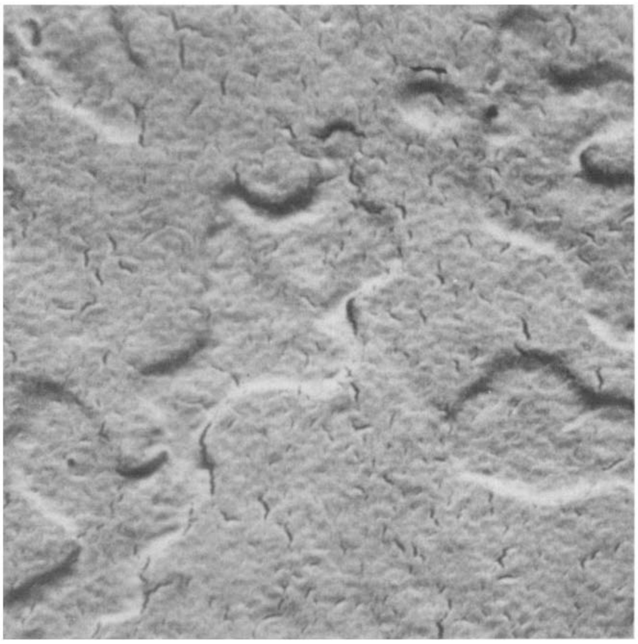

Figure 2 **The surface of crosslinked PE with 61% of gel fraction (magnification x6000)**

$$x=\frac{\rho-\rho_a}{\Delta\rho}$$

where ρ is density of the sample, ρ_a density of the amorphous phase$=0.854$ g cm^{-3}, ρ_c density of the crystalline phase

$$\Delta\rho=\rho_c-\rho_a=0.143$$

Electron microscopy

The micrographs were taken using a JEOL ISM-S1 scanning electron microscope. Samples were broken in the frozen state at -186°C. The fracture surface was covered by gold in a vacuum.

X-ray

The X-ray measurements were performed in a cylindrical camera of radius 114 mm, using the CuKα radiation filtered with Ni foil. The samples were used in the form of foils. The interplanar distances d_{110}, and d_{200}, degree of crystallinity and the relative dimensions of crystals $(D/D_0)_{110}$ and $(D/D_0)_{200}$ were calculated. The studies were carried out for the XLPE samples and the corresponding samples annealed for 6 h in boiling water[7].

N.m.r.

The n.m.r. measurements were carried out using a pulse n.m.r. spectrometer Bruker SXP4/100. The T_2 spin–spin relaxation time and the fraction of short relaxing polymer have been determined. The details concerning methods of measurements and calculation are given in the paper[8].

RESULTS

The relation between the gel fraction and the concentration of peroxide used for crosslinking is shown in *Table 1*. The gel fraction is high and shows no extrema, it increases slightly with considerable increase in the peroxide content.

Changes in the density of XLPE with an increase in peroxide content are presented in *Table 2*. The data show a maximum density of 0.5% of peroxide. The effect is more visible in the case of the degree of crystallinity calculated from the density (*Table 2*).

Similar results, except the maximum density were obtained by other authors[3,4]. The electron microscope image of uncrosslinked PE (*Figure 1*) appears as the usual lamellar morphology pattern[9]. The crosslinked PE with 61% gel (*Figure 2*) reveals shallow cavities, some foldings, microcracks and large flat cavities. To the contrary, the fracture surface of the XLPE with 91% gel does not reveal such large cavities (*Figure 3*) but only small convexities probably due to the presence of ZnO clusters.

The number of bonds between two PE chains as a

Figure 3 **The surface of crosslinked PE with 91% of gel fraction (magnification x6000)**

Table 3 Number of peroxide molecules associated with two PE chains. Symbols as for *Table 1*

	Number of peroxide molecules per 2 PE chains		Number of peroxide molecules per 2 PE chains		Number of peroxide molecules per 2 PE chains	Concentration of peroxides
1	2	3	4	5	6	7
1a	0.294	2a	0.280	3a	0.276	0.5
1b	0.588	2b	0.559	3b	0.552	1
1c	0.882	2c	0.839	3c	0.828	1.5
1d	1.176	2d	1.119	3d	1.103	2
1e	1.471	2e	1.399	3e	1.379	2.5

Table 4 Crystallinity of crosslinked polyethylene (normal samples). Symbols as for *Table 1*

Type of peroxide (%)	0	1	2	3
0	0.331	–	–	–
0.5	–	0.347	0.317	0.327
1	–	0.365	0.328	0.332
1.5	–	0.364	0.304	0.32
2	–	0.345	0.285	0.292
2.5	–	0.326	0.240	0.298

Table 5 Crystallinity of crosslinked polyethylene (annealed samples). Symbols as for *Table 1*

Type of peroxide (%)	1	2	3	4
0	0.387	–	–	–
0.5	–	0.375	0.397	0.396
1	–	0.410	0.411	0.376
1.5	–	0.361	0.331	0.367
2	–	0.354	0.366	0.370
2.5	–	0.367	0.358	0.340

Table 6 Interplanar distance d_{110} (normal samples). Symbols as for *Table 1*

Type of peroxide (%)	0	1	2	3
0	4.13	–	–	–
0.5	–	4.11	4.12	4.10
1	–	4.16	4.14	3.98
1.5	–	4.13	4.15	3.95
2		4.12	4.14	4.00
2.5		4.15	4.13	4.11

Table 7 Interplanar distance d_{200} (normal sample). Symbols as for *Table 1*

Type of peroxide (%)	0	1	2	3
	3.76	–	–	–
0.5	–	3.73	3.74	3.72
1	–	3.76	3.76	3.60
1.5	–	3.75	3.76	3.60
2	–	3.74	3.75	3.60
2.5	–	3.77	3.74	3.74

Table 8 Interplanar distance d_{110} (annealed samples). Symbols as for *Table 1*

Type of peroxide (%)	0	1	2	3
0	4.135	–	–	–
0.5	–	4.16	4.11	4.11
1	–	4.12	4.09	4.08
1.5	–	4.12	4.10	4.07
2	–	4.11	4.11	4.08
2.5	–	4.11	4.00	4.05

Table 9 Interplanar distance d_{200} (annealed samples). Symbols as for *Table 1*

Type of peroxide (%)	0	1	2	3
0	3.73	–	–	–
0.5	–	3.71	3.73	3.73
1	–	3.71	3.84	3.71
1.5	–	3.73	3.72	3.71
2	–	3.72	3.72	3.66
2.5	–	3.73	3.66	3.68

function of peroxide content was stoichometrically calculated. Based on previous work[6] it was assumed that one peroxide molecule, independently of the number of peroxide groups, is responsible only for one bond between two PE chains. The calculations were based on the following equation:

$$A=\frac{x\cdot M_{\mathrm{PE}}}{m_{\mathrm{per}}}$$

where: A is the number of peroxide molecules per two PE chains, M_{PE} the molecular weight of PE, m_{per} the molecular weight of peroxide (in this case dicumyl peroxide), x the mass concentration of peroxide per one gram of PE.

As can be seen in *Table 3*, starting at 2% concentration, one molecule of peroxide is associated with two polyethylene chains. The degree of crystallinity values determined by X-ray method (normal) XLPE and annealed XLPE are shown in *Tables 4* and *5*. Comparing these results we can see that after annealing the crystallinity increases, although the effect of the type of peroxide is diminished. *Tables 6* and *7* indicate the dependence of interplanar distance d_{110} and d_{200} for normal samples. Only for Luperox 101 are these parameters slightly different from the others. In the case of annealed XLPE (*Tables 8* and *9*) values of d_{hkl} decrease as the concentration of peroxide increases.

The interplanar distances of four diffraction lines appearing in the chosen region of the X-ray diffraction

Table 10 Interplanar distance (*d*) and Bragg angles (*Q*). Symbols as for *Table 1*

0		1		2		3	
Q	*d*	*Q*	*d*	*Q*	*d*	*Q*	*d*
29.76	3.002	29.76	3.002	29.14	3.064	29.14	3.064
–	–	31.44	2.845	31.44	2.854	31.39	2.850
–	–	34.14	2.626	34.09	2.630	34.09	2.630
35.78	2.510	35.90	2.501	35.94	2.499	35.83	2.505

Table 11 Relative size of XLPE crystals in the diffraction (110 and 200) in comparison with the size of uncrosslinked PE. Symbols as for *Table 1*

Symbol	Peroxide (%)	$D/D_{0\,110}$	$D/D_{0\,200}$
PE	0	1.0000	1.0000
1a	0.5	0.9661	1.1242
1b	1	1.0892	0.9679
1c	1.5	1.0892	0.9679
1d	2	1.0118	1.1529
1e	2.5	1.0240	0.9679
2a	0.5	1.0240	1.0226
2b	1	1.0621	1.1830
2c	1.5	1.0892	0.9235
2d	2	1.0240	0.9679
2e	2.5	1.0892	1.0838
3a	0.5	1.0621	0.9679
3b	1	0.9144	1.0226
3c	1.5	1.0240	0.9235
3d	2	1.0240	0.8380
3e	2.5	1.0755	1.0838

Table 12 Ratio of annealed crystal size to the normal crystal size, s, normal samples; w, annealed samples. Symbols as for *Table 1*

Symbol	Peroxide (%)	$D_w/D_{s\,110}$	$D_w/D_{s\,200}$
PE	0	0.966	1.058
1a	0.5	1.127	0.712
1b	1	0.940	0.850
1c	1.5	0.940	1.222
1d	2	1.076	1.000
1e	2.5	0.977	1.222
2a	0.5	1.012	0.922
2b	1	0.953	0.797
2c	1.5	0.975	1.000
2d	2	0.988	0.974
2e	2.5	0.887	0.811
3a	0.5	1.013	0.995
3b	1	1.081	0.941
3c	1.5	0.965	1.107
3d	2	0.965	0.847
3e	2.5	1.013	0.893

pattern are shown in *Table 10*. As can be seen, two of them are missing for uncrosslinked PE. Values of the relative crystal size are shown in *Table 11*. We can see that they do not change remarkably compared with the size of the uncrosslinked PE crystal. *Table 12* indicates the ratio of the annealed XLPE cyrstal size to that of normal XLPE crystal size. There are minor differences between these sizes of crystals.

Additional information was obtained from n.m.r. investigation by calculating spin–spin relaxation times T_2 at 25°C and 45°C as functions of peroxide concentration (*Figures 4* and *5*). The temperature 45°C was chosen to investigate changes of XLPE structure at the α relaxation zone, previously determined by mechanical methods[1,2,7]. *Figure 4* illustrates the relation between the short relaxation time T_2' and peroxide concentration at 25°C. The short spin–spin relaxation time T_2' at 25°C is shorter for the uncrosslinked PE than for XLPE and reveals two distinctive extrema.

One extremum occurs in the range between 0.5 and 1% of peroxide concentration, the other at 2%.

A similar relation was found at 45°C (*Figure 5*), except that the value of T_2' for uncrosslinked PE is higher than for XLPE. Additionally the extrema on this plot are inversed as compared with the behaviour at 25°C.

Long spin–spin relaxation time T_2'' dependences on peroxide concentration at 25°C and 45°C are shown in *Figures 6* and *7*. The value of T_2'' at 25°C generally drops with increase in peroxide concentration. However, some maximum in the range of 1% of peroxide content is observed. At 45°C T_2'' is steadily falling with increase in peroxide concentration (*Figure 7*).

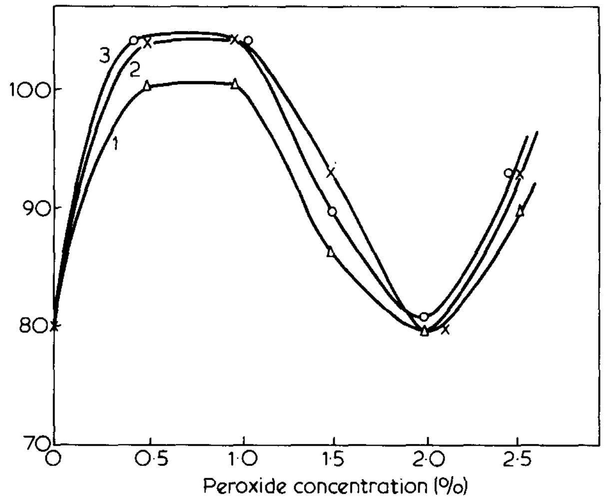

Figure 4 Relation between short relaxation time spin–spin T_2' for crosslinked PE and peroxide concentration, at 25°C

Additionally the fractions of material with short relaxation times are shown in *Figures 8* and *9* for 25°C and 45°C, respectively. It is seen that generally at both temperatures the parameter f is decreasing with the increase in peroxide concentration, except the appearance of extrema at 25°C.

DISCUSSION

It is important to point out that the proportionality between gel content and concentration of peroxide does not exist at large concentrations. In our experiment the amount of peroxide used probably creates additional

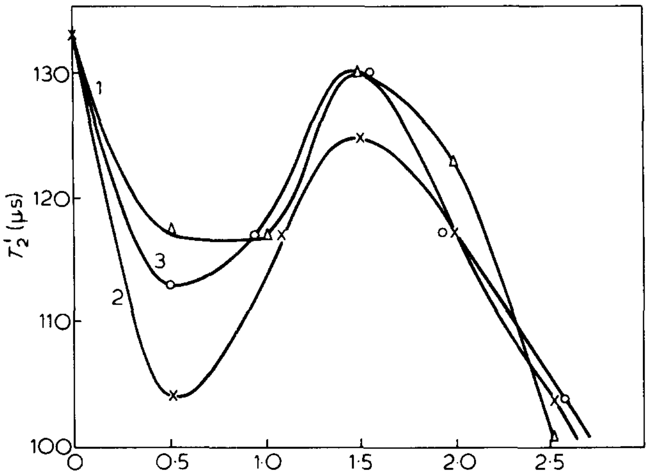

Figure 5 Relation between short relaxation time spin–spin T_2' for crosslinked PE and peroxide concentration at 45°C

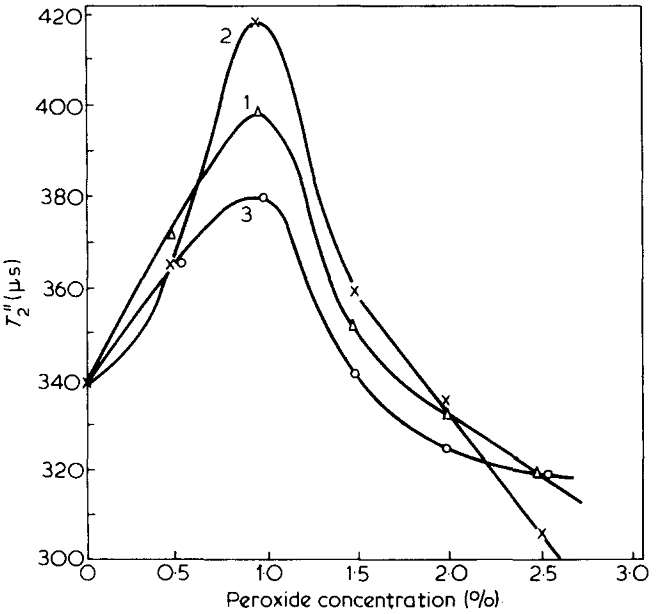

Figure 6 Relation between long relaxation time spin–spin T_2'' for crosslinked PE and peroxide concentration at 25°C

bonds between PE chains, producing excessive bonding or degradation without changing the gel content (*Figures 4–6, 8*). The decrease of the XLPE density is similar to that observed for slightly crosslinked PE and for irradiated PE[5], with the exception that we found the maximum density in the range of 0.5% peroxide concentration. The decrease in density may be due to additional branching introduced by peroxide.

The appearance of a crystallinity maximum at 0.5% of peroxide concentration was also detected in our previous dynamic mechanical investigation[1,2]. It is, however, impossible to explain this phenomenon on the basis of our present investigation. We can only suggest that some appropriate amount, or type, of peroxide degradation products in some range of the magnitude of PE chains mobility are acting as a nuclei and are producing excessive crystallinity.

The steady drop in crystallinity as a function of peroxide concentration is produced by the same mechanism as the decrease in density. Additionally the reason could be that the increasing amount of gel or crosslinks impose some restraint on mobility of the polymer chains in the molten state preventing them from arranging into lamellae folds.

Annealing the XLPE shows that adequate space for chain movement, and creation of nuclei still exists in XLPE. Subsequently the additional crystallization is possible.

Assuming that the annealed samples are closer to the equilibrium state than the normal samples, one could conclude that the chemical character of peroxide does not

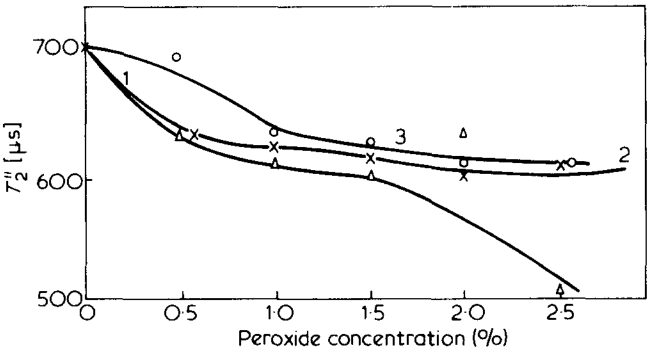

Figure 7 Relation between long relaxation time spin–spin T_2'' for crosslinked PE and peroxide concentration at 45°C

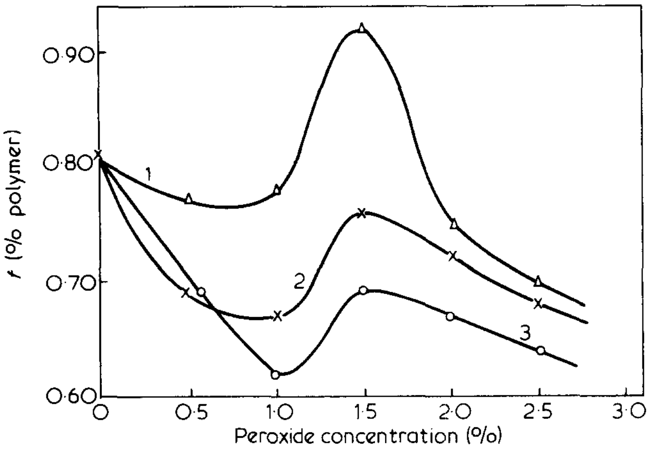

Figure 8 Relation between fraction with short relaxation time in crosslinked PE and peroxide concentration at 25°C

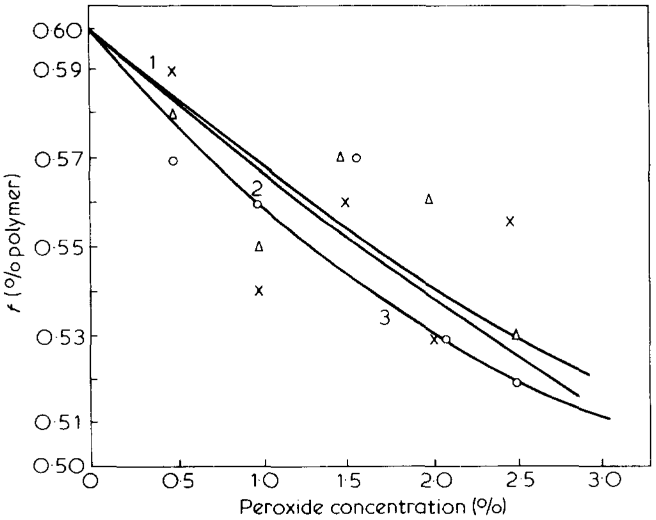

Figure 9 Relation between fraction with short relaxation time in crosslinked PE and peroxide concentration at 45°C

exert much influence on equilibrium state, but is probably responsible for the kinetics of crystallization.

Some deformation of the unit cell existing before and after annealing (*Table 10*) suggests that different peroxides produce slightly different topology of polyethylene networks, which in the molten state impose minor changes in the unit cell of XLPE. There also exists a possibility that some part of the network or network defects are built into the half molten lamellae. From *Tables 11* and *12* we can conclude that the crosslinking introduces only slight changes in the dimension of the crystals.

The appearance of big flat cavities only in the XLPE with 61% gel (*Figure 2*) could be due to the existence of some separate phase in moderately crosslinked PE. This phase could possibly be attributed to the PE network or to the uncrosslinked amorphous phase of PE. In trying to explain the phenomena observed earlier[1,2], n.m.r. studies were indispensable. According to Charlesby[4] the short relaxation time T_2' represents entanglements and networks in crosslinked polymers. This part of the polymer we called the hard amorphous phase in XLPE. The long relaxation time T_2'' represents short chains[4] or network defects in crosslinked polymers, which could be called the soft amorphous phase of XLPE.

To a similar extent, two phases in PE have been found by Zachman[10] and Schneider *et al.*[11]. It has to be pointed out that the extrema found out in the relation between T_2' and the peroxide concentration are located at the same peroxide concentration as the extrema obtained from dynamic mechanical investigations of XLPE with small strains[1,2]. It seems that an increase in crystallinity at 0.5% peroxide produces a decrease in the density of the hard amorhous phase which might be responsible for the observed maximum of the relaxation time T_2'. Similar phenomena with the amorphous phase have been observed in nylons[9]. Formation of a uniform network at 2% peroxide indicated by stoichometric calculation, decreases the molecular weight between the junctions and consequently produces a minimum T_2'.

Beyond this range of peroxide concentration this compound probably produces degradation of the network or chains and the density of the network decreases, which in turn, might be responsible for an increase in T_2'. The different behaviour of T_2' as a function of peroxide concentration observed at 45°C (*Figure 5*), has its origin in the structure of the crystallinities, which play the main role in the α relaxation range of XLPE. To our mind the process is connected with the folds on the lamella surface or changes inside lamella, but not by the amorphous phase itself.

The minimum of the function $T_2'=f$ (% peroxide) in 0.5% concentration of this compound could be related to an increase in the density of folds, which accompanies the increase in crystallinity in this range. The maximum of this function within the 1.5 to 2.0% of peroxide, could be explained by the decrease in fold density, due to a crosslinking reaction between the folds. The proposal that each fold in PE crystals can react chemically has been proved by Keller[9].

The T''^2 maximum at 25°C *Figure 6* could not be explained. The fall in T_2'' with the increase in peroxide concentration (*Figures 6* and *7*) could be associated with the increase in the amount of short chains or network defects, because of peroxide side reactions.

An interesting conclusion could be drawn from the analysis of the relation between the fraction of the polymer f with the short relaxation time and peroxide concentration at both temperatures (*Figures 8* and *9*). The amount of hard phase decreases with increase in peroxide content. This means that the soft phase prevails when the crosslinking process takes place in the presence of a large amount of peroxide in PE. This phenomenon plays a significant role in the formation of static mechanical properties of crosslinked PE[1,2,14,15].

CONCLUSION

(i) The concentration of peroxide plays the major role in the building of the different structures in crosslinked low density polyethylene.

(ii) The gel content, crystallinity and changes in crystal unit cell dimensions depend on the type and content of peroxide.

(iii) In our crosslinked polyethylene we have found two distinct structures. The maximum crystallinity at 0.5% peroxide and probably a regular network in the range of 2% peroxide.

(iv) The n.m.r. investigation appears to be the most reliable method for establishing the structures in crosslinked PE.

The existence of a hard and soft amorphous phase in XLPE is assumed. The values of short relaxation spin-spin time are different at 25°C and 45°C. This effect might be associated with the changes in free volume. Similar behaviour was found in crosslinked polypropylene[12,13].

The nuclear magnetic phenomena, we think, plays a significant role in the formation of not only the static but also the dynamic mechanical properties of crosslinked polyolefines[14,15,16].

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