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Polyethylene Unit Cell and Crystallinity Variations as a Consequence of Different Cross-Linking Processes

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ABSTRACT: Changes of crystallinity and unit cell parameters for a low-density polyethylene as a consequence of cross-linking by dicumyl peroxide and by electron beam irradiations are compared. Polyethylene samples cross-linked by irradiation in the solid state present variations essentially only of the *a* unit cell parameter while those cross-linked in the melt state present similar variations of both *a* and *b* unit cell parameters. A strict analogy with unit cell variations observed for ethene random copolymers with propene and with bulkier comonomers, respectively, is shown. This suggests inclusion of cross-links for solid-state cross-linked samples, which would lead to a gradual transformation from an orthorhombic to a pseudohexagonal phase, and exclusion of cross-links for melt state cross-linked samples, which would generate tensions at the orthorhombic crystallite interphases.

Introduction

Both high-density and low-density cross-linked polyethylenes have become commonly used industrial polymers. In fact, the cross-linking of polyethylene molecules into three-dimensional networks leads to significant improvements of material properties. Compared with the untreated material, cross-linked polyethylene shows enhanced impact strength, better thermal performance, and higher chemical resistance. Further considerable improvements can be found for the wear and creep behavior and for aging characteristics.[1,2]

Currently, different techniques are in use for production of cross-linked polyethylene; the most common technique is the radical cross-linking[3,4] initiated by peroxide or via β, γ, or electron beam irradiation.[5] Different techniques[6−8] comprise vinylsilane grafting to the polymer chains, after initiation with a small amount of added peroxide, followed by cross-linking at 80−90 °C at 100% relative humidity or in water.[9,10]

Several studies relative to crystallization and morphology[11−23] of cross-linked polyethylene have shown that network density strongly influence crystallization rate, degree of crystallinity, and lamellar thickness. However, only few studies have considered variations of the unit cell parameters generated by cross-linking processes.[24−28]

Large variations of the unit cell parameter *a* (up to 15%) of the polyethylene orthorhombic unit cell[29] (with *b* and *c* remaining substantially constant) have been reported by Ungar and Keller[25] for high-density polyethylene cross-linked by γ-radiation. In particular, hexagonal lattice symmetry for high radiation doses is approached ($a \rightarrow b\sqrt{3}$). A hexagonal phase for cross-linked polyethylene was also reported by Orth and Fischer[26] for single-crystal samples irradiated in an electron microscope at elevated temperature.

Essentially negligible unit cell variations have been instead reported for low-density polyethylene samples cross-linked using several peroxides at low concentrations.[27] However, substantial and comparable increases of *a* (2.3%) and of *b* (2.9%) unit cell parameters have been reported for a low-density polyethylene sample cross-linked by high dicumyl peroxide concentrations (~7%).[28]

In the present paper, changes of crystallinity and unit cell parameters for a low-density polyethylene as a consequence of cross-linking by dicumyl peroxide and by electron beam irradiations are compared.

Experimental Section

Materials. As for chemical cross-linking, the used polymer was a low-density polyethylene containing 2% of dicumyl peroxide and 0.2% of an antioxidative agent (4,4′-thiobis(*ter*-butyl-5-methylphenol)), whereas for cross-linking by irradiation, the used polymer was the same low-density polyethylene containing only the antioxidative agent. These two commercial samples include a low-density polyethylene with a density of 0.918 g/cm^3 and a melt flow index close to 2. Samples containing dicumyl peroxide (DCP) at different concentrations (used for chemical cross-linking at temperature close to melting, see point iii below) have been accomplished by adding the required amount of dicumyl peroxide to previously heated polyethylene pellets at 70 °C for 2 h.

Polyethylene sheets, thickness ~250 μm, used for irradiation procedures and used as reference un-cross-linked samples, have been obtained by compression molding. Irradiation has been carried out in air with electrons of 1.1 MeV accelerated in a linear “S” band accelerator (3.0GHz), produced by Irvin Electronica S.p.A. and used for industrial cable production. The current beam was 1 mA, and the dose rate was roughly estimated as ~15 Mrad/min.

Three sets of chemical cross-linked samples have been analyzed: (i) sheets (thickness ~250−450 μm) cut by a microtome from high-voltage cables, cross-linked at ~180 °C; (ii) sheets (thickness ~500 μm) obtained by compression molding at 180 °C for different times; (iii) films (thickness ~100 μm) obtained by compression molding at ~120 °C of samples with dicumyl peroxide content of 1 or 2 or 4 wt %.

The gel fraction has been determined as the percent of the original weight of the sample after extracting for 6 h in boiling decahydronaphthalene. The extraction, according to the ASTM method,[30] has been followed by drying at 150 °C in a vacuum oven.

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X-ray diffraction patterns have been obtained with an automatic 1710 Philips powder diffractometer using a Ni-filtered Cu Kα radiation. A measure of crystallinity index has been obtained by resolving the X-ray diffraction patterns, for the range $10° < 2\theta < 40°$, into the diffraction area relative to the crystalline peaks (I_c) and relative to the amorphous halo (I_a):

$$X_{c,R} = \frac{I_c}{I_c + I_a} \times 100$$

Evaluation of the correlation length D of the crystalline domains, in a direction perpendicular to the chain axis, has been effected by using for the main equatorial reflection the Scherrer equation:

$$D_{110} = 0.9\lambda/\beta \cos \theta_{110}$$

where β is the half-maximum line breadth. For $\beta < 1.0°$ (in 2θ units) the procedure described in ref 31 for the correction of the half-width for experimental effects was applied. In particular, we used a standard quartz specimen having a half-maximum line breadth, under similar geometrical conditions, of 0.15°.

Calorimetric measurements have been carried out on a DSC 2920 apparatus manufactured by TA Instruments, in flowing N_2, with heating rate of 10 °C/min. The melting temperatures and the heats of fusion have been evaluated from the peak temperatures and the areas of the maxima of the appropriate endotherms. The crystallinity index ($X_{c,D}$) has been calculated, as in ref 32, by using the melting enthalpy of an infinite size polyethylene orthorhombic crystal (($\Delta H^0_m = 280$ J/g).[33]

Infrared spectra have been obtained at a resolution of 2.0 cm^{-1} with a Bruker-Vector 22 FTIR spectrometer in the range 4000−400 cm^{-1}.

The carbonyl ratios have been determined, as usual, by calculating the ratios of the peak height of the ketone band at 1717 cm^{-1} to that of a reference band at 2022 cm^{-1}, corresponding to methylene vibration in both crystal and amorphous regions and independent of crystallinity of the polymer.[34,35]

Results

X-ray diffraction patterns of an un-cross-linked PE sample (A) and of samples cross-linked by irradiation (B) or by peroxide (C) are shown in Figure 1. The diffraction profiles show typical peaks relative to the crystallographic planes (110), (200), and (020) of the orthorhombic form of polyethylene[29] superimposed on the amorphous halo.

The sample cross-linked by irradiation (Figure 1B), presenting a gel fraction of 89%, shows a larger shift of the 200 reflection with respect to the shift of the 020 reflection (compare curve B with curve A of Figure 1). This corresponds to a larger increase of the unit cell parameters a (1.75%) and minor increase of the unit cell parameter b (0.4%).

The chemically cross-linked cable sample (Figure 1C), presenting a gel fraction of 67%, shows, instead, comparable shifts of all crystalline peaks toward lower 2θ values that correspond to comparable increases of a and b unit cell parameters of the orthorhombic unit cell of polyethylene (of nearly 2%).

Unit cell parameters a and b for all considered samples are reported versus the gel fraction in Figure 2.

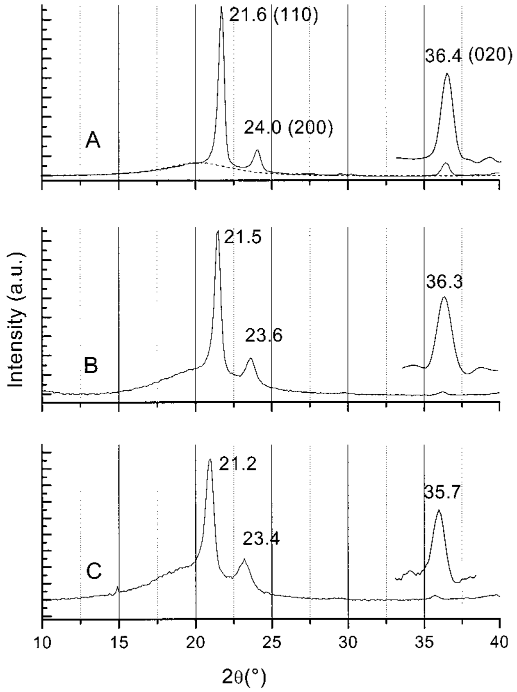

Figure 1. X-ray diffraction profiles of an un-cross-linked PE sample (A) and of samples cross-linked by irradiation (B) or by peroxide (C). The gel fractions of samples B and C are 89% and 67%, respectively. The dashed line indicates the amorphous diffraction.

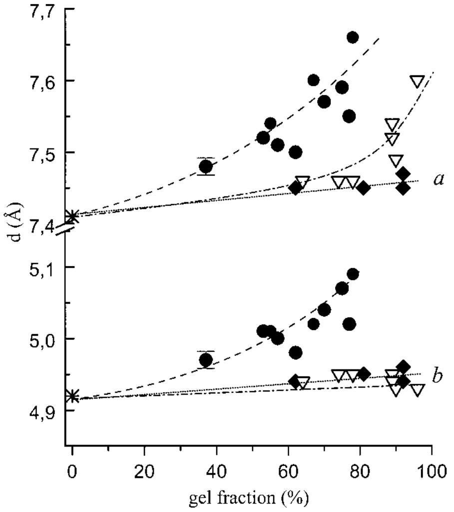

Figure 2. Unit cell parameters a and b for samples chemically cross-linked at 180 °C (●) and 120 °C (◆) and cross-linked by irradiation (▽) versus the gel fraction.

For samples chemically cross-linked in the melt at 180 °C (filled circles), substantial and comparable increases of both crystallographic axes are observed with increasing the degree of cross-linking (gel fraction). On the other hand, for samples cross-linked by irradiation (emptied triangles) large increases only for the a axis are obtained.

Crystallinity indexes evaluated by X-ray diffraction measurements ($X_{c,R}$) and evaluated by DSC measurements ($X_{c,D}$) on samples chemically cross-linked at 180 °C and cross-linked by irradiation are reported versus the gel fraction in Figures 3 and 4A, respectively.

The melting temperatures (T_m) evaluated for the same samples by calorimetric measurements are reported versus the gel fraction in Figure 4B.

It is apparent that the crystallinity indexes and melting temperatures of chemically cross-linked samples gradually decrease with increasing the gel fraction. The crystallinity indexes and melting temperatures of irradiated samples, instead, remain almost constant for gel fraction lower than 80%.

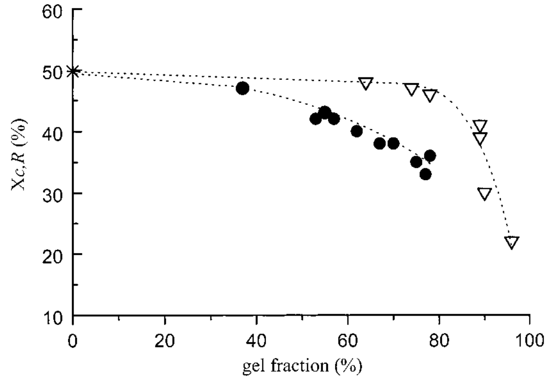

Figure 3. Crystallinity indexes evaluated by X-ray diffraction measurements ($X_{c,R}$) on samples chemically cross-linked at 180 °C (●) and cross-linked by irradiation (▽) versus the gel fraction.

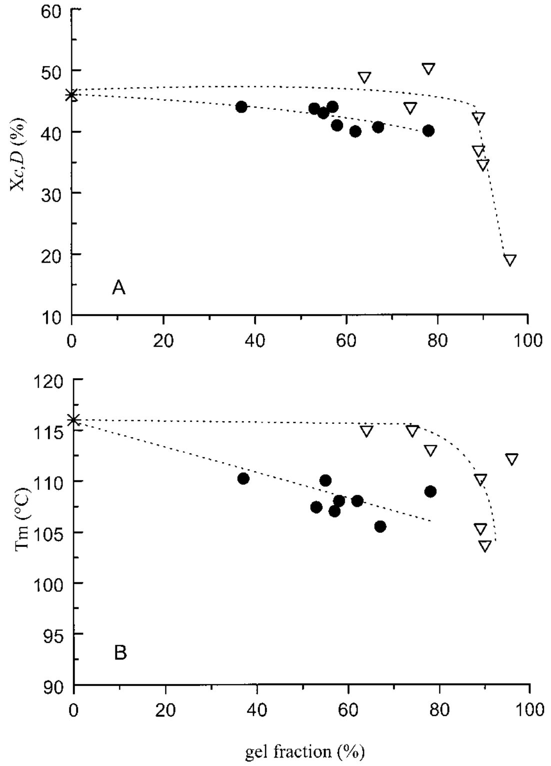

Figure 4. Crystallinity indexes ($X_{c,D}$) evaluated by calorimetric measurements (A) and the melting temperatures (T_m) (B) on samples chemically cross-linked at 180 °C (●) and cross-linked by irradiation (▽) versus the gel fraction.

It is however worth noting that the decrease of the degree of crystallinity with increasing the degree of cross-linking, measured by DSC measurements, is less pronounced than observed by X-ray measurements. In particular, as for chemically cross-linked samples, $X_{c,R}$ decreases from 49% down to 33% (Figure 3) while correspondingly $X_{c,D}$ decrease only from 46% to 41% (Figure 4A). This behavior can be interpreted by the occurrence of recrystallization phenomena during the calorimetric scan. In fact, for instance, by DSC measurements at 40 °C/min, $X_{c,D}$ decreases for the same samples from 43% to 33%. Analogous differences between crystallinity data obtained using X-ray diffraction and DSC measurements were not observed by previous studies relative to chemically cross-linked samples.[24,28]

The correlation length D relative to 110 reflection (D_{110}) presents a behavior similar to that one described for crystallinity indexes and melting temperatures. In fact, for chemically cross-linked samples the D_{110} values gradually decrease, with increasing the gel fraction, from ~255 to ~165 Å, whereas for irradiated samples, the D_{110} values remain almost constant at least for gel fraction lower than 80%.

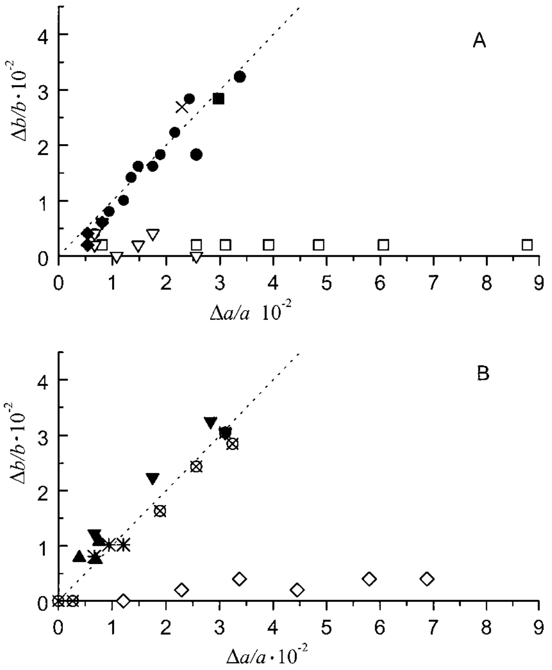

Figure 5. Percent variations of a and b unit cell parameters for (A) cross-linked polyethylene samples by irradiation ((▽) present paper, (□) ref 25) or by chemical cross-linking with dicumyl peroxide ((●) at 180 °C, (◆) at 120 °C present paper, (×) ref 28) or by peroxide and vinylsilane (■) and (B) ethene random copolymers with propene ((◇), ref 37), with 1-octene ((▲, ▼, ⊗), refs 38−40), and with styrene ((∗), ref 36).

It is well-known that when polyethylene is irradiated in the presence of oxygen, free radicals (mostly alkyl radicals) are produced which react with oxygen to yield ketones, producing an FTIR peak at 1717 cm^{-1}.[14,34] The measured carbonyl ratios evaluated by FTIR measurements for cross-linked samples are generally in the range 1.2−2.0, except for those irradiated at high radiation doses, presenting gel fractions larger than 80%, in which the carbonyl ratios increase up to 8.

These oxidation phenomena well account for the steep decreases of crystallinity (Figures 3 and 4A), melting temperatures (Figure 4B), and correlation length observed for samples irradiated at high radiation doses, presenting gel fractions larger than 80%.

As for samples chemically cross-linked at 120 °C (filled diamonds in Figure 2), although a high degree of cross-linking can be reached (up to 92%), very low increases of a and b unit cell parameters (lower than 1%) are observed. Correspondingly, substantially negligible variations of crystallinity and of correlation length of the crystalline domains are also observed.

Discussion

The percent variations of a and b unit cell parameters for cross-linked polyethylene samples, as measured in the present paper and as taken from the literature,[25,28] are compared in Figure 5A. Filled symbols correspond to chemically cross-linked samples, while empty symbols correspond to samples cross-linked by irradiation in the solid state. As for chemical cross-linking, besides present data (filled circles and diamonds), also the single data taken from Kao and Phillips[28] (cross), as well as data relative to a commercial sample cross-linked after vinylsilane grafting (filled square), are reported.

Samples cross-linked by irradiation show increases of *a* unit cell parameter while the *b* unit cell parameter remains essentially constant. This result holds also for our samples irradiated in air at higher radiation doses, presenting gel fractions larger than 80% and a high carbonyl ratio.

On the other hand, all chemically cross-linked samples show similar increases of both *a* and *b* unit cell parameters. Lower increases have been observed for samples cross-linked by peroxide at 120 °C (filled diamonds), for which crystal regions are poorly affected by cross-links, whereas larger increases (up to 3.5%) have been observed for samples chemically cross-linked in the melt (filled circles).

For the sake of comparison, the percent variations of *a* and *b* unit cell parameters as measured by X-ray diffraction patterns of ethene random copolymers are shown in Figure 5B. In particular, data relative to ethene random copolymers with propene,[37] with 1-octene,[38-40] and with styrene[36] are shown.

These data show similar variations of the unit cell parameters *a* and *b* for the case of comonomer units bulkier than propene.[38,41-44] On the other hand, for ethene–propene copolymers, unit cell parameter *a* markedly increases with increasing the propene content, whereas the *b* and *c* axes remain practically constant.[37,42,45-47]

The distortions observed for the orthorhombic lattice of polyethylene in the presence of bulk comonomer units could be due to tensions at the crystallites interfaces produced by the presence of bulky side groups confined to the neighbor amorphous regions.[48] On the other hand, the increase of unit cell parameter *a* up to $a \cong b\sqrt{3}$, (that is, up to $\Delta a/a \cong 15\%$) with increasing the propene content is due to the gradual transition from the orthorhombic crystalline phase toward the hexagonal crystalline phase.[37,42,45-47] This transition is associated with at least partial inclusion of methyl group into the crystalline lattice of polyethylene.[48]

The strict analogy between the plots of Figure 5A,B suggests that a similar interpretation could be given for both phenomena.

In particular, the increases of both *a* and *b* crystallographic axes observed for chemically cross-linked samples can be rationalized with the exclusion of the constitutional defects (cross-links) from the crystalline lattice of polyethylene. In fact, the exclusion of the cross-links would generate tensions at the crystallite interphase, as the exclusion of bulky substituents for ethene random copolymers.

On the other hand, larger increases of the crystallographic *a* axis with respect to the *b* axis, observed for samples cross-linked by irradiation in the solid state, can be rationalized with the inclusion of the cross-links into the crystalline lattice of polyethylene. In fact, the inclusion of the cross-links would lead to a gradual transformation from orthorhombic to pseudohexagonal phase, as the inclusion of methyl substituents of ethene–propene copolymers. This interpretation is consistent with the earlier and more pronounced reduction of crystallinity (Figure 3), of correlation length of the crystalline domains, and of melting temperature (Figure 4) which are observed, with increasing degree of cross-linking, for samples cross-linked in the melt state with respect to samples cross-linked in the solid state.

To verify this interpretation, all the samples cross-linked by irradiation have been melted at 180 °C for 60 min and then crystallized on cooling to room temperature.

Well-detectable decreases of melting temperatures, of crystallinity indexes, and of coherent length have been observed. For instance, for the sample of Figure 1B presenting a gel content of 89%, a variation of melting temperatures from 115 to 99 °C, of crystallinity indexes $X_{c,R}$ from 41% down to 31%, and of coherent length D_{110} from 223 to 102 Å have been observed. Analogous variations as a consequence of melting and crystallizations were observed by Gielenz and Jugnickel for linear polyethylene cross-linked by irradiation with fast electrons in the solid state.[24]

As a consequence of melting and recrystallization of samples cross-linked by irradiation in the solid state, decreases of *a* unit cell parameters (average decrease of 0.02 Å) and increases of the *b* unit cell parameters (average increase of 0.02 Å) are observed. These observations are consistent with at least partial exclusion of cross-links from the crystalline polyethylene phase, produced by melting and recrystallization.

The very small increases of both crystallographic axes *a* and *b* observed for samples chemically cross-linked at 120 °C (Figures 2 and 5A) are consistent with cross-links essentially excluded not only from the crystalline phase but also from the crystallite interphases. In fact, in this case, the chemically cross-links would occur essentially only into the amorphous phase, while the crystalline phase (as well as the crystalline–amorphous interphase) would be preserved by cross-linking due to their poor molecular mobility at a temperature very close to the melting temperature.

Conclusions

Polyethylene samples cross-linked by irradiation in the solid state present large variations of the *a* unit cell parameters while the *b* and *c* parameters of the orthorhombic unit cell remain substantially unaltered. On the other hand, polyethylene samples cross-linked in the melt state present similar variations of *a* and *b* unit cell parameters.

A strict analogy between variations of unit cell parameters observed for polyethylene samples cross-linked in the solid state and in the melt state and those observed for ethene random copolymers with propene and with bulkier comonomers, respectively, has been shown.

This suggests inclusion of cross-links for solid-state cross-linked samples, which would lead to a gradual transformation from orthorhombic to pseudohexagonal phase, as the inclusion of methyl substituents of ethene–propene copolymers. On the other hand, exclusion of cross-links for melt state cross-linked samples would generate tensions at the crystallite interphase, as the exclusion of bulky substituents for ethene random copolymers.

This interpretation is consistent with the lower crystallinity, size of crystalline domain, and melting temperature observed for samples cross-linked in the melt state as well as with substantial reduction of the same properties as a consequence of melting and recrystallization of samples cross-linked in the solid state.

Samples chemically cross-linked at temperature close to the polyethylene melting temperature present only very small increases of *a* and *b* unit cell parameters consistent with cross-links essentially excluded not only from the crystalline phase but also from the crystallite interphases.

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