Polymer Bulletin 3, 305-310 (1980)

Polymer Bulletin

Degradation of Nitric Acid-Treated Bulk Polyethylene

2. Selective Removal of Chain Defects

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Summary

The Selective removal of Chain Defects (branches, unsaturations) by nitric acid from melt crystallized polyethylene is examined with reference to the question of the distribution of defects between crystalline and "amorphous" domains. The results obtained using the IR methyl band at 1376 cm^{-1} together with weight-loss measurements support the view that the majority of defects, which are situated in the non-crystalline regions, are selectively digested by the nitric acid attack. After removal of the non-crystalline phase the small remaining branch content located within the crystal cores confirms the levels of defect inclusion previously derived from unit cell expansion data.

Introduction

In a preceding study (BALTA-CALLEJA, GONZALEZ ORTEGA and MARTINEZ-SALAZAR, 1978) we have proposed a method for the quantitative evaluation of the concentration of chain defects within the polyethylene (PE) lattice based on a model which takes into account the penetration of constitutional defects (branches, unsaturations etc) at interstitial crystal sites by means of a generation of 2g1 step chain defects (kink isomers). The samples investigated were mainly low density PE's that had been crystallized from the melt with butyl or larger side sequences. The expansion of the unit cell was explained by assuming that a fraction of molecular defects, smaller than 20%, was accomodated within the lattice. The majority of the defects (>80%), admittedly due to their large size (BALTA-CALLEJA and HOSEMANN 1980), are thought to be rejected from the crystals. This conclusion has been also shown to apply for isothermally crystallized samples (MARTINEZ-SALAZAR and BALTA-CALLEJA, 1980^{a}). Recent statistical calculations (MARTINEZ-SALAZAR and BALTA-CALLEJA, 1980^{b}) based on X-ray crystallinity and crystal thickness data are, in addition, consistent with these defect inclusion results. The purposes of the present contribution are: 1) to investigate the selective removal of chain defects by fuming nitric acid (FNA) treatment in order to confirm in a conclusive and independent manner the previous data on the distribution of defects between crystalline regions and non-crystalline domains. 2) To find out whether the concentration of chain defects within the crystals after prolonged FNA attack is in agreement with data derived from the expansion of the unit cell. In part I of these series (RUEDA, CAGIAO and BALTA-CALLEJA) an IR investigation on the nature and location of oxidized groups introduced by nitric acid of PE was reported.

Experimental

The work has been carried out on three selected PE samples characterized previously with different defect concentrations (RUEDA, BALTA-CALLEJA and HIDALGO, 1974 1979) (See table I). The samples were prepared from the melt pressing the polymer between 2 glass plates and cooling it at room temperature. The sample thickness was of ~1mm. Degradation with FNA was performed at 60°C in open tubes during reaction times between 5-180 h. After a specific time the sample was diluted, filtered and washed in distilled water. Finally it was rinsed in a Soxhlet extractor for 6 h with acetone and dried thereafter in vacuo. Due to the powdery appearance of the samples after long treatment times (>50h) the KBr method was mostly used for the IR study, thus the samples were dissolved in ethylene tetrachloride and KBr was added to the solution at a ratio 100-600:1. The solvent was allowed to evaporate and the residue ground and compressed in a disk form. Three samples were also prepared in the form of thin films in order to double check the IR data obtained with KBr method. The IR spectra were recorded using a Perkin Elmer 457 Spectrophotometer. Measurements of branch content (given in number of methyl groups per 100 carbon atoms) were made using the methyl band at 1376 cm^{-1} in the infrared spectrum following the procedures described in preceeding papers (BALTA-CALLEJA and HIDALGO, 1969; RUEDA, BALTA-CALLEJA and HIDALGO, 1979). Weight loss values were derived from the weight of the samples before and after treatment. They are given as the ratio ΔP, of the change in weight of the sample to the weight of the sample before treatment.

Results and Discussion

Fig. 1 illustrates the rapid decrease of the total chain defect content (branches), for the three samples investigated as a function of the FNA treatment time. It is noteworthy that the data obtained with the BrK disk method (solid symbols) and with thin films (open symbols) are indistinguishable from each other. After 50-60 h of treatment time the defect content falls for samples 1 and 2 from 1.8 and 3.5% to values in the range of 0.6-0.7%. Although the 1376 cm^{-1} band can be

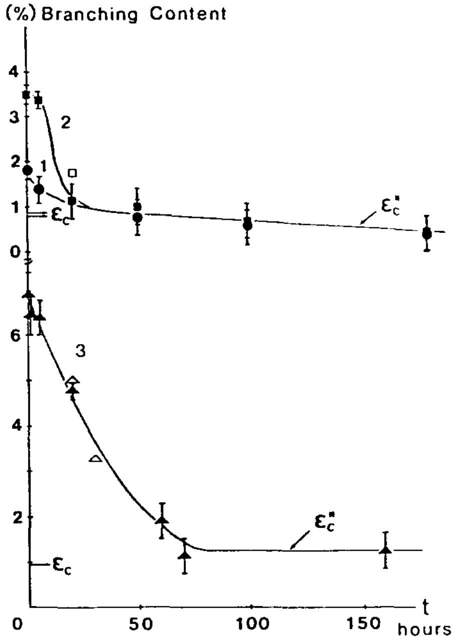


Fig. 1. Branching content (from IR) as function of treatment time with FNA.

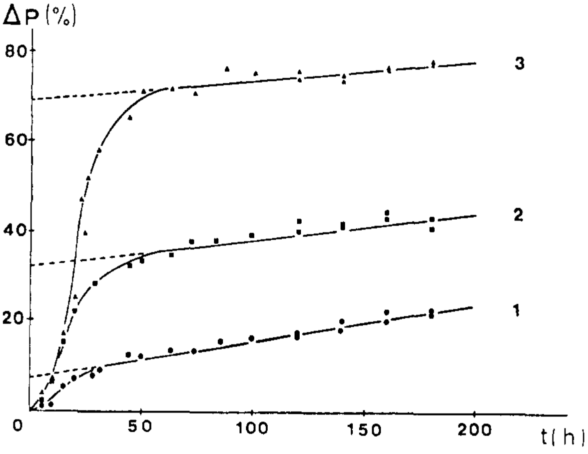


Fig. 2. Weight loss in per cent of original weight as function of exposure time to FNA.

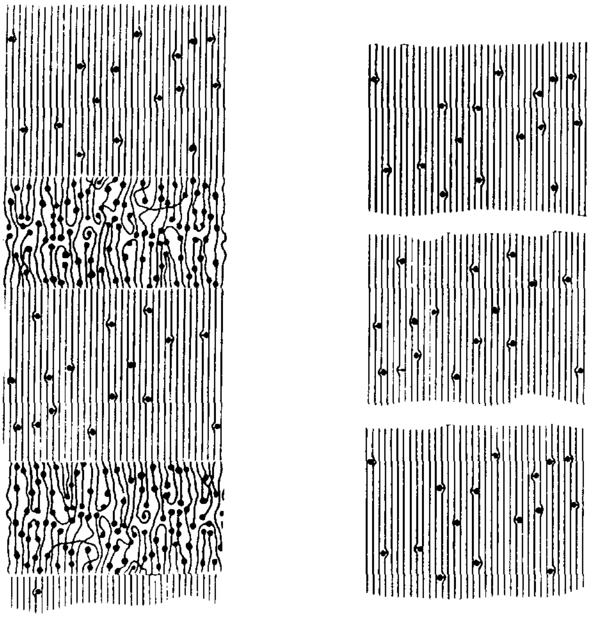
TABLE I

Molecular weight, FNA crystallinity, unsaturation content, branching content, total defect content ($\varepsilon_{C=C}+\varepsilon_{-CH_3}$), defect content within crystals, (from unit cell measurements), defect content within crystals (from IR), for the three polyethylene samples investigated

Sample	$M_w.10^{-3}$	α(%)	$\varepsilon_{C=C}$(%)	ε_{-CH_3}(%)	ε(%)	ε_c(%)	ε_c^* (%)
1	12.0	93	0.27	1.54	1.8	0.79	0.6±0.2
2	9.5	68	0.43	3.06	3.5	0.83	0.7±0.2
3	11.0	31	0.18	6.72	6.9	0.96	1.2±0.3

still distinguished for treatment times larger than 100 h the quantitative estimate of branch content becomes difficult in this case due to the high background. For sample 3, the branching content falls from 6.9 to ~1.2%. In the same time about 10%, 35% and 70% of the material was respectively lost for the three samples. These changes shown in Fig. 2 yield a valuable information on the morphology. The interpretation of data is based on the assumption that the non-crystalline regions are more accesible to the acid than the cores so that after a given time (in our case ~50 h) only the better crystallized domains are preserved (BLUNDELL and KELLER, 1967). It is further reasonable to expect that those defects localized at the surface disordered layers and at lateral grain boundaries will be, as a result, more susceptible to FNA attack than defects occluded within the crystals (HOLDSWORTH and KELLER, 1969). Due to the lower density of the amorphous phase the initial rate of weight loss (Fig. 2) is markedly larger in the samples with a higher "amorphous" content, 1-α. (The latter value is straightforwardly derived from the intercept of the slope for the smaller weight loss rate). However, the oxidation of the disordered regions ends up earlier for the less defective (t~40 h) than for the more defective samples (t~60 h). This is evidently so because the volume fraction of amorphous material is notably smaller in the former than in the latter case. After the amorphous domains have been removed the weight loss rate, owing to the impenetrability of the crystal lattice, is dramatically reduced (10-500 times). Comparison of the results from Figs. 1 and 2 leads to the following conclusions:

1) Initially (t<50 h) the rate loss of chain defects is approximately equal to the rate loss of material. This favours the view that these defects are largely



(a) (b)

Fig. 3. Schematics of the distribution of chain defects between crystalline lamellae and "amorphous" layers a) before and b) after prolonged FNA exposure.

situated in the non crystalline regions (Fig. 3a) as suggested in previous papers (BALTA-CALLEJA, GONZALEZ ORTEGA and MARTINEZ-SALAZAR, 1978). 2) The limiting value of ε (after 50 h), when the amorphous layer has been digested, lies between 0.6 and 1.2%. This means that a small, but nevertheless detectable, fraction of defects, that we shall call, ε_c^*, still remains within the crystal cores after prolonged FNA attack (Fig. 3b). 3) The final smaller weight loss rate in Fig. 2 is nearly indistinguishable for the three investigated samples - having a similar density of ε_c^* defects (Table I) - indicating that the impenetrability of the lattice is very nearly the same in these cases. This result supports the presence of branch points firmly occluded at interstitial lattice sites in contrast to the concept of "amorphous" defects which would be more readily accesible to the oxidative attack. 4) The leveling off values of ε_c^* (derived from IR data) agree within the error of exparimental with the level of defect inclusion, ε_c, derived from the unit cell volume, V_ε, according to: $\varepsilon_c = (V_\varepsilon - V_0)/4\Delta V$ (BALTA-CALLEJA, GONZALEZ ORTEGA, MARTINEZ-SALAZAR, 1978) (where V_0 is the unit cell volume for $\varepsilon = 0$ and $\Delta V = 60$ Å^3 represents the excess volume of unit cell per each 2g1 kink).

This result is consistent with the view of a fairly regular distribution of defects within the crystals.
5) Since $\varepsilon_c^* \sim \varepsilon_c$ we also conclude that the number of defects in the form of unsaturations contributing to the unit cell expansion is negligible. This is partly due to the fact that the level of unsaturations is notably smaller than that of chain branching (See table I).
To sum up, the present results obtained on FNA etched PE (with butyl or larger branches) are in support of a majority of defects excluded from the lattice. In addition the IR measurements performed on the degradation debris furnish an independent confirmation on the level of defect inclusion in the PE crystalline cores favouring the concept of a regular accommodation of a small fraction of chain defects (mainly branches) within the PE crystal lattice by means of a generation of 2gl kinks.

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Received October 8, 198o
Accepted October 1o, 198o

Responsible for the text: The Editors (see inside title page of this issue). For advertisements: L. Siegel, Kurfürstendamm 237, D-1000 Berlin 15, Tel. (030) 882 1031, Telex 01-85411,
Springer-Verlag Berlin Heidelberg New York
Printed in Germany by Beltz Offsetdruck, Hemsbach/Bergstraße