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# THERMOOXIDATIVE DEGRADATION OF CROSSLINKED POLYETHYLENE

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## ABSTRACT

The thermal behaviours of the crosslinked low-density polyethylene were examined by TG and DTA.

The comparison of the thermooxidative degradation of polyethylenes with the different crosslinking degree suggests that the cross-bonds are formed on the secondary carbons of polyethylene chain.

## INTRODUCTION

A long time has been considered that the places of the chain branching ( the tertiary carbons ) of PE are not resistant to the radicals action and they are conducive to the crosslinking. Not before in the paper [1] it was ascertained that the chain branching is the steric hindrance which impedes the crosslinking. In the present work the thermooxidative degradation of polyethylenes with the different crosslinking degree has been examined and a question of the cross-bonds forming in PE is discussed.

## EXPERIMENTAL

The unstabilized LDPE Politen 2/020/FO, made at "Blachownia" Chemical Works (Poland), was examined. Five mixtures of PE with the different amounts (0.1 - 2.0 wt %) of dicumyl peroxide (Hercules, Netherlands) were made by the rolling method at 120°C.

The mixtures were crosslinked three times independently (using a Mettler TA 2000 A DTA apparatus) by the heating from the room temperature to 200°C at a heating rate 6°C/min in flowing argon. The exothermic effects of the crosslinking process were observed. The gel content in

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the crosslinked samples (50 mg) was determined by the xylene extraction. The samples (9 mg) were examined also by TG, using a Mettler TA 2 and by DTA, using a Mettler TA 2000 A thermal analysers. The analyses were made at a heating rate 6°C/min in flowing air; the pure (without peroxide) PE was examined too.

## RESULTS AND DISCUSSION

The TG curves of the crosslinked PE (2.0 wt % peroxide) ——— , and the pure PE - - - - are shown in Fig.1.

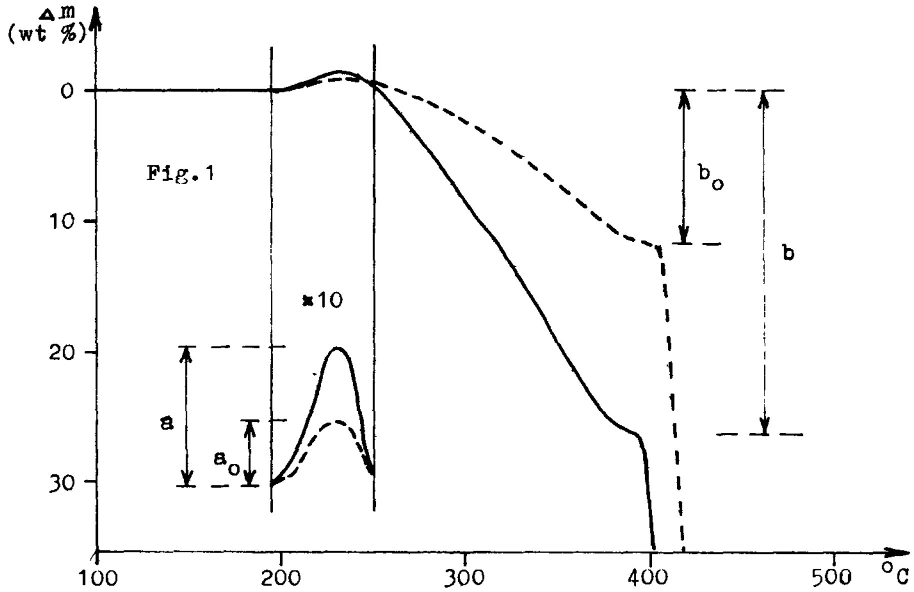
Fig.1

Fig.2 shows the DTA curves (at the range of the oxidation process only) of the crosslinked PE (2.0 wt % peroxide) ———, and the pure PE - - - -.

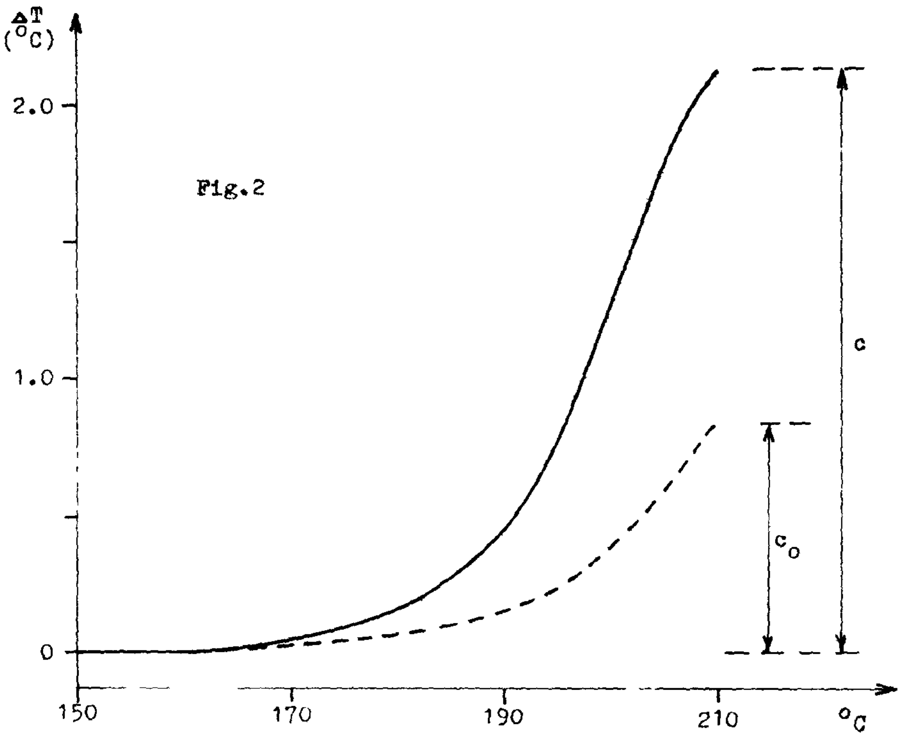

Fig.2

It is seen, that the weight increase ("a" in Fig.1) and the exothermic effect ("c" in Fig.2) which are related to the forming of the hydroperoxide links (oxidation process) as well as the weight loss of the first stage of the degradation (up to about 400°C, "b" in Fig.1) are greater in the crosslinked PE than in the pure PE ($a_o$, $b_o$, $c_o$). The first stage of the degradation is attributed to the breaking of weak links, which are mainly hydroperoxides, and to the isolation of the low molecular weight hydrocarbons and the oxygen compounds. Thus this stage of the degradation is a consequence of the previous oxidation process.

The values of $a/a_o$, $b/b_o$ and $c/c_o$ have been assumed as the characterizations of the oxidation process and the first stage of the degradation of crosslinked PE. The results are given below:

| peroxide (%) | gel (%) | $a/a_o$ | $b/b_o$ | $c/c_o$ |
|---|---|---|---|---|
| 0.1 | 10.5 | 2.44 | 1.58 | 1.19 |
| 0.3 | 25.3 | 2.81 | 1.71 | 1.45 |
| 0.6 | 57.5 | 3.26 | 1.72 | 1.71 |
| 1.0 | 71.2 | 4.07 | 1.84 | 2.05 |
| 2.0 | 87.3 | 4.56 | 2.28 | 2.58 |

It is easy to see, that when the crosslinking degree increases, the quantity of oxygen absorbed to polymer chain increases too and the oxidation process is intensive more and more.

It is well-known that the oxidation reactions of PE occure in the places of the chain branching, i.e. on the tertiary carbons [2] . As it has been ascertained that the oxidation process proceeds more intensive for the PE with the higher crosslinking degree it gives the conclusion that the quantity of the tertiary carbons increases during the crosslinking process. It indicates that the cross-bonds are formed on the secondary carbons of the polyethylene chain.

## REFERENCES

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2 L.Reich, S.S.Stivala, Autoxidation of hydrocarbons and polyolefins. M.Dekker, New York 1969