Degradation of HDPE and LLDPE in closed mixing chamber: a comparison
II. Changes of some physical and mechanical properties

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Summary
HDPE and LLDPE (containing n-butyl branches) were degraded in a closed mixing chamber. After degradation some physical and mechanical properties were investigated as a function of the chemical structure of the polymers. The effect of degradation was found different for the two materials.

Physical and mechanical properties of HDPE depend strongly on crystallization conditions and chemical irregularities of the polymer chain. The most pronounced change in physical properties was found as an effect of oxygen incorporation into the polymer at the beginning of the process. Tensile properties of the samples have shown rapid destruction after the yield point.

Physical and mechanical properties of LLDPE reveal much less dependence on crystallization conditions and changes of the chemical structure. Chemical changes caused by degradation of the polymer do not essentially change the degree of crystallinity under the conditions investigated. Chain breaking of the polymer results in a slight decrease in the tensile properties, which can be attributed to the decrease in the number of tie-chains.

Introduction
In our previous paper (1) changes of the chemical structure of linear high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) caused by degradation during moulding in a closed mixing chamber were studied and the degradation mechanisms of the two polymers were compared. In the present work changes in some physical and mechanical properties as a function of those in the chemical structure are discussed.

Experimental Materials
Measurements were carried out on additive free fluff samples of Marlex 6001 type HDPE and Marlex TR 125 type LLDPE containing 6.5 n-butyl branches per 1,000 carbon atoms (Phillips products). The two types of polymers have similar molecular masses and Melt index values (see Ref. (1)).

Sample preparation, procedure
The materials were moulded in the mixing chamber of a
Rheocord EU 10-V plasticorder (HAAKE, Inc., USA) at 200 °C chamber temperature with 50 rpm for different periods of time. From the moulded materials samples were prepared by a) quenching in liquid nitrogen and b) pressing at 200 °C and then cooling slowly. For detailed description see Ref. (1).

Investigations

The properties studied and the methods used are summarized in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical structure</td>
<td>IR spectroscopy, titrmetry, extraction</td>
<td>See Ref. (1)</td>
</tr>
<tr>
<td>Density</td>
<td>Gradient column</td>
<td>23 °C; mixtures of ethanol and benzyl alcohol</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>DSC</td>
<td>10 °C/min heating rate</td>
</tr>
<tr>
<td>Yield stress</td>
<td>Tensile test</td>
<td>Room temperature; 100 mm/min drawing rate</td>
</tr>
<tr>
<td>Ultimate strength and elongation</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Results

Chemical changes of HDPE and LLDPE as an effect of degradation in a closed mixing chamber were discussed in detail in our previous paper (1). In the course of degradation oxygen was built into both polymers, mainly in ketone form. At the beginning of the degradation the rate of oxidation was found to be faster for LLDPE than for HDPE but later this relation was reversed. Degradation in a closed mixing chamber, i.e., at low oxygen concentration, can be regarded as thermal degradation induced by oxygen (2). During degradation of LLDPE chain scission processes predominate, while in the case of HDPE, as a result of recombination reactions of alkyl radicals, chain linking can also be observed.

Physical properties of the two polymers are different due to the differences in their chemical structure and morphology. Changes of the chemical structure caused by degradation during moulding induce also changes in the physical and mechanical properties of the resultant solid polymer. These latter changes were studied as a function of the concentration of "chemical irregularities", i.e., of groups differing from -(CH<sub>2</sub>)<sub>n</sub> homogeneous structure. In this sense butyl side branches of LLDPE were also taken as chemical irregularities. Concentrations of all the irregular groups determined (total carbonyl-, hydroperoxide-, unsaturated groups and CH<sub>3</sub> end-groups) were summa-