

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
Properties studied and methods used

Property	Method	Conditions
Chemical structure	IR spectroscopy, titrimetry, extraction	See Ref. (1)
Density	Gradient column	23 °C; mixtures of ethanol and benzyl alcohol
Crystallinity	DSC	10 °C/min heating rate
Yield stress	Tensile test	Room temperature; 100 mm/min drawing rate
Ultimate strength and elongation	"	"

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 $-(CH_2)_n$ 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 CH₃ end-groups) were summa-

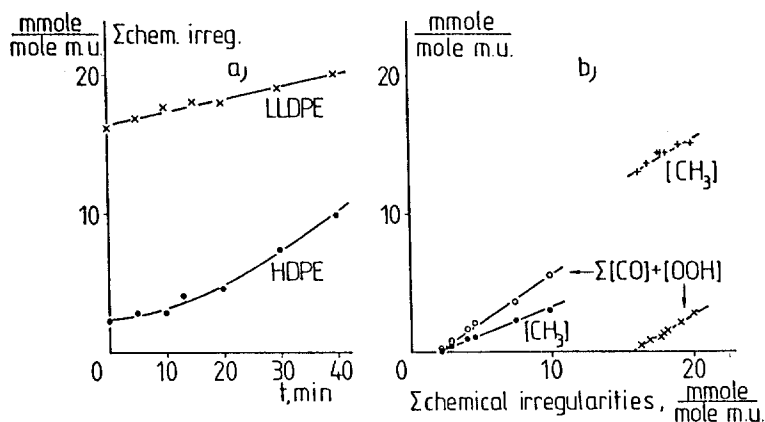


Fig. 1
Changes in the chemical structure of polyethylenes as an effect of degradation in a closed mixing chamber
a): Concentration of "chemical irregularities" vs moulding time;
b): Concentration of oxygen containing

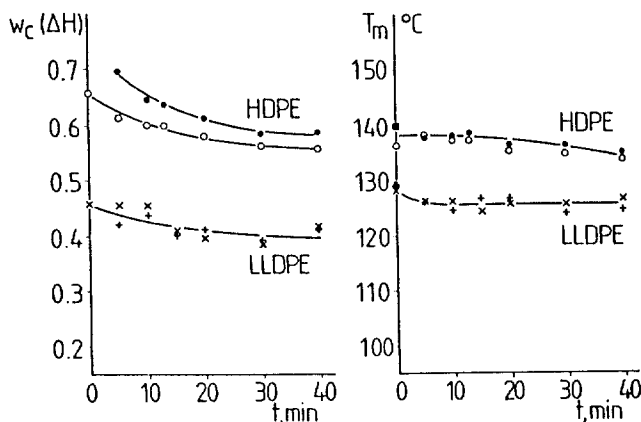
groups ($\Sigma[\text{CO}]+[\text{OOH}]$) and methyl groups ($[\text{CH}_3]$) vs concentration of "chemical irregularities". o and \bullet : HDPE; + and x: LLDPE

riized ($\Sigma[\text{CI}]$) and plotted as a function of moulding time in Fig. 1.a. The relationship is linear for LLDPE, while it has an accelerating character for HDPE.

In Fig. 1.b concentrations of oxygen containing groups and those of methyl groups are plotted as a function of $\Sigma[\text{CI}]$. These relationships are linear. The slope of the change of oxygen containing groups is the same for both polymers. In the case of LLDPE concentration of CH_3 groups and that of oxygen containing groups change similarly. The concentration of CH_3 groups in HDPE increases less with chemical irregularities than that of oxygen containing groups.

The degree of crystallinity (w_c) of quenched and pressed samples determined by DSC (3) and the melting temperature (T_m) determined at the maximum of the endothermic peak are plotted in Fig. 2 as a function of moulding time. The degree of crystallinity of HDPE strongly depends on crystallization conditions, whereas that of LLDPE does not. This result is in agreement with the literature data, which proved that the degree of crystallinity of HDPE decreases with the increasing rate

Fig. 2 Degree of crystallinity (w_c) determined from enthalpy of fusion and temperature at the endothermic peak maximum (T_m) vs moulding time. o and +: quenched samples; \bullet and x: pressed samples; \blacksquare and \blacklozenge : values given by the manufacturer.



of cooling (4,5), and thermodynamical properties of ethylene- α -olefin copolymers are independent of the cooling rate (6).

With increasing moulding time the degree of crystallinity of both polymers decreases. The change is smaller and scattering of the values is higher for LLDPE than for HDPE. It can also be seen that the difference in the degree of crystallinity of the quenched and pressed HDPE samples decreases with increasing moulding time.

T_m values of quenched HDPE are somewhat lower than those of pressed samples but maximum deviation is lower than 2 °C. In the case of LLDPE scattering of the values measured is higher than the differences caused by different cooling rates. T_m values given by the manufacturer of the polymers investigated are also shown in Fig. 2. In the case of LLDPE it corresponds to the measured value. For HDPE lower T_m was measured, which can be attributed to different sample preparation. T_m values of HDPE samples moulded for different periods of time show some decrease after 15 min moulding. Melting temperature of LLDPE remains constant after an initial small decrease.

Density values of pressed samples are plotted as a function of moulding time in Fig. 3. The trends of changes are different for the two polymers. Density of HDPE considerably decreases after short moulding time, then it tends to reach equilibrium value. Density of LLDPE shows some increase.

Yield stress of the pressed HDPE and LLDPE samples showed linear relationship with density, independently of the chemical structure, in accordance with the literature data (7,8).

In Fig. 4 ultimate tensile stress and elongation are plotted as a function of moulding time. For comparison values of stabilized samples moulded for 20 min with 50 rpm (9) are also shown in the figure. The additive free HDPE samples broke shortly after the yield point in each case, thus ultimate tensile stress was determined by the values of elongation at break. There are great differences between the values of stabilized and additive free HDPE samples. Values of additive free LLDPE samples showed considerably less decrease as compared to stabilized ones. Tensile properties of LLDPE are independent of the initial change of chemical structure, and some decrease could be detected only after 15 min moulding time.

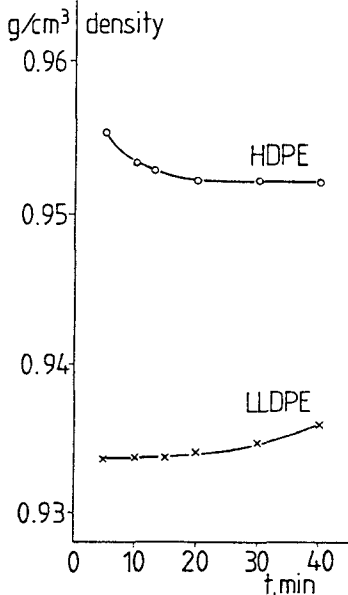


Fig. 3 Density of pressed samples vs moulding time

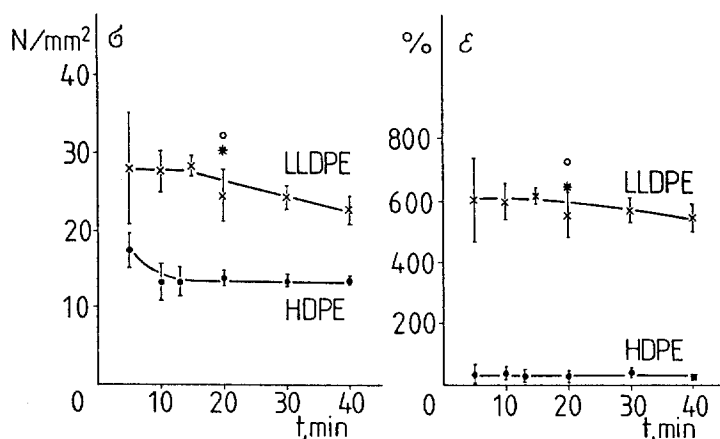


Fig. 4 Tensile strength (σ) and elongation at break (ϵ) vs moulding time. x and o: additive free samples; o: stabilized HDPE; *: stabilized LLDPE

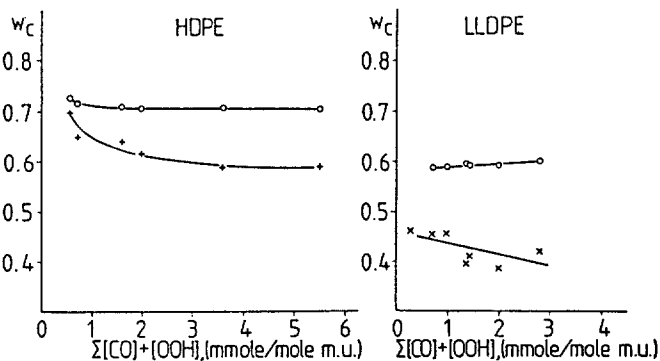
Discussion and conclusions

On the bases of the results, we may conclude that chemical changes caused by degradation in a closed mixing chamber do not have the same effect on the physical and mechanical properties of HDPE and LLDPE investigated after moulding. Properties of HDPE change more severely than those of LLDPE.

Degrees of crystallinity determined from the enthalpy of fusion (3) and from density values (10) are plotted in Fig. 5 as a function of the concentration of oxygen containing groups. For HDPE both methods gave the same tendencies: 1) with increasing oxygen content the degree of crystallinity decreases; 2) greatest changes can be found at low oxygen concentrations. With increasing concentration of oxygen containing groups the difference between the values measured by different methods increases: the degree of crystallinity calculated from density shows less decrease than that measured by DSC. These results suggest that building of oxygen into the linear polyethylene chain even in small concentration results in a less dense supermolecular structure of HDPE. Melting enthalpy decreases due to the change of the ratio of crystalline and amorphous phases. Lower decrease in the values determined from density can be attributed partly to the difference in the mass of oxygen and hydrogen atoms.

Presumably it compensates, to a certain extent, the density decrease

Fig. 5 Degree of crystallinity determined from enthalpy of fusion (+ and x) and from density (o) vs concentration of oxygen containing groups



caused by loosening of the structure.

Crystallinity values of LLDPE measured by different methods do not change in the same way as those of HDPE. The degree of crystallinity calculated from DSC data decreases with increasing oxygen content, although, to a lower extent than in the case of HDPE, and scattering of the measured values is higher. In the study of the degradation of stabilized LLDPE, also density (and the degree of crystallinity calculated there from) increase was experienced (9). Considering the amount of built-in oxygen it was found that the increase of density with increasing oxygen content can be attributed to the mass difference of oxygen and hydrogen atoms, up to 10 mmole/mole m.u. carbonyl group concentration there is no volume change as compared to the unoxidized material. This suggests that the crystalline content of LLDPE containing butyl side branches does not change essentially as an effect of chemical changes within the range investigated. Density increase is caused by the mass increase due to the oxygen atoms present. Decrease of the enthalpy of fusion may be caused by the incorporation of keto groups into the lattice (11).

In Fig. 6 the degree of crystallinity and melting temperature of quenched and pressed samples are plotted as a function of the total concentration of irregular groups measured. The degree of crystallinity changes similarly with $\Sigma[CI]$ and with the concentration of oxygen containing groups (see Fig. 1.b).

In the range investigated melting temperature of HDPE decreases linearly with increasing $\Sigma[CI]$. T_m of LLDPE reveals only some slight change but these values are considerably lower than could be expected from extrapolation of those of HDPE. The melting temperature of crystallites depends not only on the chemical composition but it is primarily determined by crystallite thickness, interfacial free energy and defects of the crystal lattice (12-17). The results shown in Fig. 6 suggest that in the range investigated, the chemical changes of

HDPE and LLDPE caused by degradation do not cause as much change in the parameters determining the degree of crystallinity and the melting temperature as induced by incorporation of the butyl side branches into the linear chain.

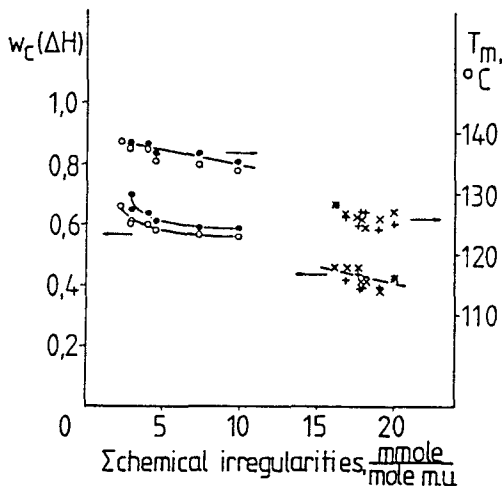


Fig. 6 Degree of crystallinity (w_c) determined from enthalpy of fusion and temperature at the endothermic peak maximum (T_m) vs concentration of "chemical irregularities". o: quenched HDPE; ●: pressed HDPE; +: quenched LLDPE; x: pressed LLDPE

Tensile properties of the two polymers also revealed different behaviours. In the measured range tensile properties of LLDPE decreased only in a relatively small extent but ultimate elongation of additive free HDPE drastically dropped in each case related to the stabilized material. This latter result was not attributed to the effect of degradation. It has been assumed that additive free and stabilized HDPE samples have different morphology: the stabilizer may act as a nucleating agent, while in the case of unstabilized samples, i.e., in the absence of any nucleating agent, larger spherulites are formed and this results in brittle fracture of the material (18). For verification of this theory, Finntalc M 15 (Finnminerals) nucleating agent was mixed to additive free HDPE in an amount equivalent to the stabilizer content of commercial material and after being moulded for 20 min under the conditions given above, the mixture was pressed into a sheet. Tensile test was carried out and 550 % elongation was found for this composition. It seems to verify the theory.

Tensile measurements of LLDPE suggest a less important effect of nucleating agents on the morphological and macroscopic properties of ethylene-1-hexene copolymer than on those of linear homopolymer. The effect of chemical changes on the mechanical properties can be tracked down not only in the case of stabilized LLDPE samples (9) but even for the additive free material. Ultimate tensile strength and elongation decrease as a result of the breaking of polymer chains during thermooxidative degradation. It indicates that the drawing behaviour of PE with butyl side branches is mainly determined by the number of tie-chains between crystallites. The slight decrease in tensile properties is most probably due to the decrease of molecular mass of the polymer, and with this, the number of tie-chains.

Summarizing the results of tensile measurements, we may draw the same conclusion as derived from changes in the physical properties: changes in the chemical structure in the range measured have smaller effect on the supermolecular structure of both polymers than caused by building side branches into the linear chain.

Acknowledgement

The authors wish to thank Phillips Petroleum Chem. for the supply of Marlex fluff samples. Thanks are expressed to Ms. V. Magyar, Mr. T. Erős and Mr. E. Tatai for the experimental work, and Mrs. É. Rudas-Gulyás and Mrs. E. Kincse for the help in preparation of the publication.

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Accepted March 18, 1988 C