

Degradation of HDPE and LLDPE in closed mixing chamber: a comparison

I. Changes in the chemical structure

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Summary

Degradation of linear high density polyethylene (HDPE) and butyl branched linear low density polyethylene (LLDPE) was studied during moulding in a closed mixing chamber. At the beginning of the process the rate of oxidative degradation was found faster for LLDPE than for HDPE but later this relation reversed. The degradation mechanism was the same for both types of polyethylenes but the rate of elementary steps depended on the chemical structure of the polymer chain. The differences were attributed to the structural differences in the original materials and the products formed during degradation.

Introduction

The properties of polyethylenes are determined mainly by the structure of the polymer chain. While the viscosity measured in melt or in solution is affected mainly by long chain branches, properties depending on crystallinity (e.g. crystalline melting point, density, hardness, permeability, etc.) are determined by the type, number and distribution of short chain branches (1). In addition to technological problems caused by the high viscosity of molten LLDPE (2-6), the question of polymer degradation during processing must also be tackled.

In our previous paper (7) the degradation of commercial stabilized LLDPE was studied. In the present work additive free polyethylenes were investigated. Changes in polymer properties caused by degradation in a closed mixing chamber (i.e. at low oxygen pressure) and the effect of the polymer chain structure on the extent and character of the changes were studied on HDPE and LLDPE containing n-butyl branches. The two polymers have similar rheological properties. The results will be published in two parts. In this one the chemical changes are described. In the second part changes of the physical and mechanical properties as a function of those of the chemical structure will be discussed.

Experimental

Materials

For the degradation studies Marlex 6001 type HDPE and Marlex TR 125 type LLDPE (Phillips products) were used in additive free fluff form. The properties of the polymers are summarized in Table 1.

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Table 1
Properties of polymers investigated

Property	Unit	ASTM method	HDPE	LLDPE
Density	g/cm ³	D 1505	0.961	0.934
Melt index 190°C, 2.16 kg	g/10 min	D 1238	0.15	0.20
\bar{M}_w			190,000	230,000
\bar{M}_n			21,000	16,500
Crystalline melting point	°C		140	129
Number of branches	$\frac{\text{branches}}{1000 \text{ C atom}}$		-	6.5 n-butyl

Sample preparation, procedure

The materials (35 g each) were moulded in the mixing chamber of a Rheocord EU 10-V plasticorder (HAAKE, Inc., USA) at 200 °C with 50 rpm for different periods of time. During moulding the torque and the temperature of the material were simultaneously recorded. Samples were prepared from the moulded material as follows: material removed from the mixing chamber was

- dropped into liquid nitrogen and stored in a deep-freezer up to investigation, in order to freeze in the intermediate products of the chemical reactions;
- pressed in argon atmosphere at 200 °C to sheets of 1 mm, then stored in a refrigerator.

Investigations

The structures determined and the methods used are summarized in Table 2.

Results

During moulding the chemical structure of unstabilized PE undergoes some changes. This is suggested by the torque vs. time curves shown in Fig. 1. It seems from the curves that during moulding in a closed mixing chamber, LLDPE suffers mainly breaking, while HDPE, after initial chain breaking reveals some increase of torque, suggesting an increase in chain length (7). For comparison, the torque vs. time curves of stabilized sam-

Table 2
Structures determined and methods used

Quantity investigated	Method	Ref.
Gel content	Soxhlet extraction in xylene	
Hydroperoxide group	titrimetry	(8)
Carboxyl group	"	(9)
Total carbonyl group	IR spectroscopy	(9)
Methyl group	"	(10)
Vinyl group	"	(11)
Trans-vinylene group	"	(11)
Vinylidene group	"	(12)

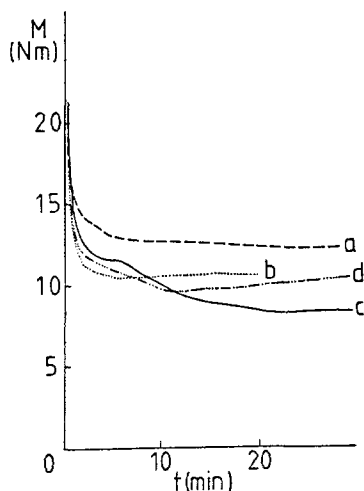


Fig. 1 Torque vs. time curves measured in a closed mixing chamber. Chamber temperature: 200°C; rotor speed: 50 rpm. a: stabilized LLDPE; b: stabilized HDPE; c: LLDPE fluff; d: HDPE fluff.

ples moulded under the same conditions are also shown in the figure. After a short period of time the torque values of LLDPE fluff become considerably lower than those of the stabilized sample (curves a and c) and the deviation further increases after 6 minutes of moulding. The difference between the torque curves of stabilized and fluff HDPE is less (curves b and d). From this figure it can also be seen that the tendency to chain breaking or chain linking is related to the polymer structure, the course of the

curves of stabilized and fluff samples is the same.

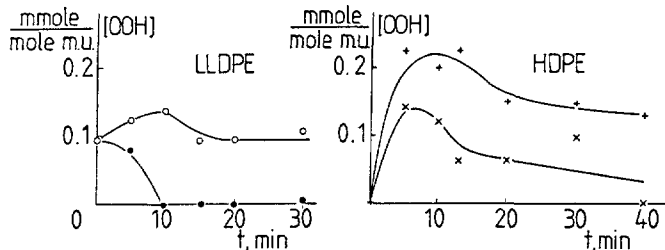
In Fig. 2 hydroperoxide concentrations of quenched and pressed samples are plotted against moulding time. Concentration of the detectable hydroperoxide group was found to be low in both polymers. Before moulding the hydroperoxide group could not be traced in HDPE, while it could be definitely detected in LLDPE. Hydroperoxide group concentration reveals a characteristic maximum curve, and the values are higher for HDPE than for LLDPE. During pressing in argon atmosphere hydroperoxide group concentration decreases considerably, similarly to the degradation of LDPE (13).

The carbonyl group concentration of pressed samples is presented in Fig. 3.a. In accordance with the literature data (14,15), the plot of total carbonyl group concentration (ECO) vs. mixing time shows that at the initial stage of moulding, the branched polymer takes up more oxygen than the linear one. Later the situation is reversed, the rate of oxygen uptake of HDPE increases considerably compared to that of LLDPE. In the IR spectra the absorption maximum of the C=O group was found at 1720 cm^{-1} , suggesting that the bulk of oxidized groups are keto groups.

According to Luongo (16) the absorption at 1410 cm^{-1} can be attributed to the C=O group built in a long paraffin chain (between two methylene groups). The relative intensities at this wave number were determined and plotted as a function of total carbonyl

group concentration in Fig. 3.b.

Fig. 2 Hydroperoxide group concentration vs. moulding time. o and + quenched samples; ● and x pressed samples.



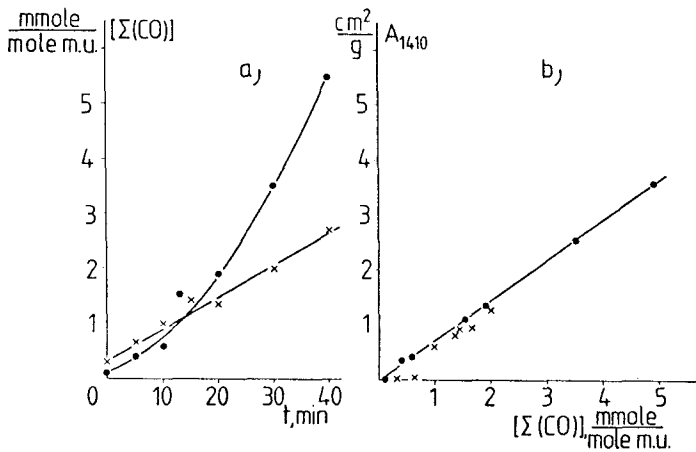


Fig. 3 a) Total carbonyl group concentration vs moulding time. b) Relative absorption of long chain ketones at 1410 cm^{-1} vs. total carbonyl group concentration. ● HDPE; x LLDPE

There is a linear relationship between the two parameters. The concentration of

the long chain ketone belonging to the same total carbonyl group concentration is nearly equal for both polymers, though the values determined for LLDPE seem somewhat lower, especially in the initial stage of oxidation.

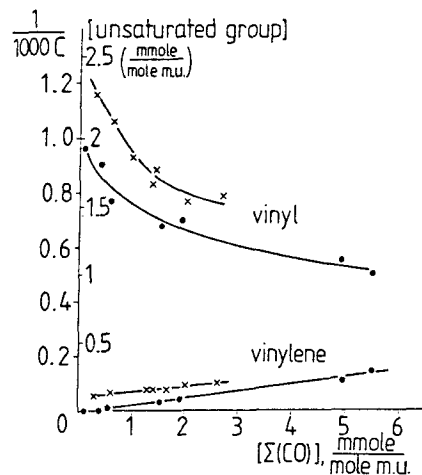
Neither of the samples revealed presence of carbonyl groups. This is not surprising since moulding was carried out at low oxygen pressure, and the carbonyl groups are formed in secondary reactions or by transformation of ROO' radicals (17).

On the basis of absorption of the samples in the range of 1000 to 850 cm^{-1} it can be stated that the unsaturated groups of HDPE consist mainly of vinyl groups and in low concentration of vinylidene groups. With increasing moulding time vinyl group concentration decreases, and trans-vinylene groups appear with increasing concentration. There are three types of unsaturated groups present in the untreated LLDPE fluff sample with higher concentration of vinyl and vinylidene groups than in HDPE. Concentration of the latter is $0.34 \text{ mmole/mole m.u.}$ in LLDPE compared to the value of $0.12 \text{ mmole/mole m.u.}$ found in HDPE.

The concentrations of vinyl and trans-vinylene groups are presented as a function of total carbonyl group concentration in Fig. 4. From the \bar{M}_n values 1.4 vinyl group per one n initial chain was calculated for both polymers.

In the initial stage of degradation vinyl concentration of both polymers decreases rapidly, then the fast decrease slows down with increasing oxygen content, and tends to reach equilibrium values. The initial rate of vinyl

Fig. 4 Concentration of unsaturated groups vs. total carbonyl group concentration. ● HDPE; x LLDPE



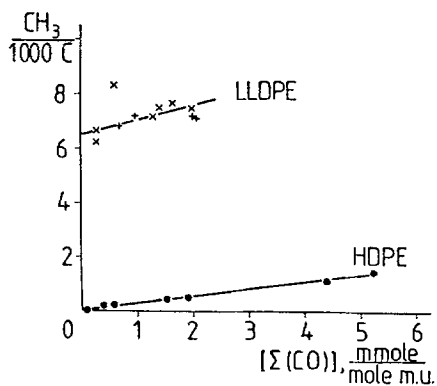


Fig. 5 Concentration of end-chain methyl group vs. total carbonyl group concentration.

group concentration decrease is higher for LLDPE than for HDPE.

The concentration of trans-vinylene group determined from the absorption at 965 cm^{-1} increases linearly with the amount of built-in carbonyl groups. The change is higher for HDPE than for LLDPE.

The concentration of vinylidene groups can be only roughly estimated from the absorption

between 900 and 860 cm^{-1} as the butyl group also absorbs light in this region. It was found, however, that actual concentration did not change significantly under the degradation conditions studied.

Concentration of CH_3 groups, calculated from absorption intensity at 1375 cm^{-1} , plotted as a function of total carbonyl group concentration is illustrated in Fig. 5. For both polymers concentration of the methyl group increases linearly with that of the carbonyl group. The slope is steeper in the case of LLDPE than for HDPE proving more intensive chain breaking of the former. From the more moderate change of CH_3 group concentration and the increase of torque measured during moulding (Fig. 1), it can be concluded that in HDPE degradation in addition to chain breaking, recombination reactions resulting in growth of the polymer chains also play a predominant role. Therefore, gel content of the samples was investigated. Insoluble gel phase could not be found in any of the samples. It must be pointed out, however, that under more severe degradation conditions (moulding with higher rotor speed) HDPE contained some insoluble gel phase, while LLDPE did not (7).

Discussion and conclusions

The chemical changes determined after the degradation of HDPE and LLDPE in a closed mixing chamber can be summarized as follows:

- 1) Breaking of the polymer chains and in the case of HDPE also some chain linking.
- 2) Oxygen incorporation into the polymer chains, mainly in the form of ketone.
- 3) Decrease in vinyl content, and consequently in total unsaturated group concentration. Formation of a small amount of trans-vinylene groups. The number of vinylidene groups is practically unchanged.

Similarly to the literature data (18) the results presented above verify the fact that the degradation mechanism of different types of polyethylenes is similar. However, two significant differences can be observed:

- 1) In the initial stage of degradation LLDPE takes up oxygen faster than HDPE, later this order is reversed.
- 2) In the degradation of LLDPE, besides oxidation, mainly chain

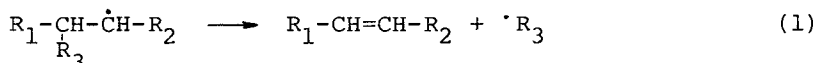
scission processes predominate. In the case of HDPE, after a certain period of time chain linking can also be observed.

Degradation in a closed mixing chamber, i.e., at low oxygen pressure, can be regarded as a thermal degradation induced by oxygen (15). The process begins with formation and decomposition of hydroperoxides but in the propagation and termination steps of the chain reaction alkyl radicals gain an increasing role.

The degradation of both polymers is initiated at the unsaturated groups, which is proved by the immediate decrease in the number of vinyl groups. The hydrogen on the α -carbon atom adjacent to a vinylidene group is less stable than that in α -position to a vinyl group (19,20), but the number of vinylidene groups in the samples investigated is by an order of magnitude lower than that of vinyl groups, therefore, the latter have an important role in the initiation process.

The diminishing of vinyl groups can be explained by the decomposition of allyl hydroperoxides, mostly by ethylene formation, but according to the literature (21) also by simultaneous formation of aldehyde groups and acetaldehyde. The decrease in the rate of vinyl group diminishing can be attributed to the fact that during degradation vinyl groups are also formed either by isomerisation of hydrocarbon radicals accompanied by chain scission or by disproportionation (22).

Vinylene group formation is a process characteristic of reactions of secondary radicals at low oxygen pressure. The mechanism of formation can be explained by recombination or isomerisation (15). Holmström and Sörvik (23) consider also the following β -scission possible:



From energetic aspects, however, scission of a hydrogen atom in α -position to the tertiary carbon atom seems less probable, owing to the lower energy of H on the tertiary carbon atom (24,25).

The fact that trans-vinylene group concentration increases faster in HDPE than in LLDPE can be attributed to the character of the formation reactions described above: in HDPE only secondary (and primary) radicals are formed before recombination of secondary radicals, while at the initial stage of LLDPE degradation even reactions of tertiary radicals not resulting in the formation of vinylene groups have an important role.

Further reactions of the radicals formed on the carbon atom in α -position to the vinylidene group do not necessarily cause disappearance of the vinylidene group (26,27). On the other hand vinylidene groups can be formed by chain scission of tertiary alkyl radicals in the course of degradation (15,23,28). The presence of tertiary carbon atoms is given in LLDPE while it is formed in recombination reactions in HDPE. This explains the practically negligible change in the concentration of vinylidene groups during degradation.

The dominating role of the reactions of alkyl radicals in the degradation carried out in a closed mixing chamber is evidenced by the lack of acid in both polymers, contrary to degradation in oxygen, where oxidation products contain great amount of carboxyl groups (17). In our case, mainly ketones were

formed.

From secondary hydroperoxides, ketones are formed without chain scission, mainly by disproportionation in the cage (29). In the case of tertiary hydroperoxide, ketone formation results always in chain scission. For LLDPE containing butyl branches the scission of the longer chain is more likely because the energy of C-C bonds decreases with increasing chain length (24). From NMR data Cheng et al (30) concluded that the probability ratio of main chain and butyl side chain scission is 2:1. This may be the explanation of minimal difference in the concentration of paraffinic carbonyl groups in HDPE and LLDPE (Fig.3.b).

Breaking of the polymer chains can be detected not only in LLDPE but in HDPE, as well. Although the effect of recombination reactions resulting in polymer chain growth is predominant after a given moulding time, chain scission processes are proved by the increase of methyl group concentration.

The observation that the rate of HDPE degradation is lower at the beginning and it is higher later than that of LLDPE, can be explained as follows.

The difference in the initial rates of degradation can be attributed to three factors. The initial rate of LLDPE degradation is higher, because 1) in the LLDPE studied the concentration of unsaturated groups and within this, the concentration of vinylidene groups is higher than in HDPE; 2) the stability of LLDPE is decreased by the presence of tertiary carbon atoms; 3) hydroperoxides can be detected in the untreated LLDPE. In the initial period of moulding hydroperoxides immediately initiate the oxidation of polymers as no induction period is needed to start PE oxidation in the presence of hydroperoxides (13). The untreated HDPE sample does not contain hydroperoxides and the concentration of vinylidene groups and tertiary carbon atoms is low.

The difference found in the mechanism of degradation after the initial stage can be explained also by the difference in the chemical structure of the two polymers. During degradation of HDPE at low oxygen pressure, the recombination of hydrocarbon radicals seems to have an important role, while in the case of LLDPE, chain scission processes predominate. In recombination reactions steric effects are essential (15). In the case of HDPE, conditions for chain linking are fulfilled, for LLDPE the observations suggest steric hindrance of the butyl side chains, so that chain breaking processes become predominant against recombination reactions.

The acceleration of HDPE oxidation related to that of LLDPE can be attributed principally to the different decomposition products of secondary and tertiary hydroperoxides. From tertiary hydroperoxides stable ketones are formed. The decomposition of secondary hydroperoxides results also in the formation of aldehydes, which contain an unstable H atom and undergo further thermal and oxidative reactions. This assumption is supported by the results of degradation in closed mixing chamber with more intensive mixing. Under the same conditions we could detect carboxyl groups in HDPE but not in LLDPE. On the other hand, the difference in oxidation rates may also be due to the change in the number of tertiary carbon atoms. These decrease gradually in LLDPE as a result of chain scission and in-

crease in HDPE upon the effect of recombination reactions.

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