Degradation Of LDPE LLDPE and HDPE In Film Extrusion

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ABSTRACT

The degradation of different polyethylenes, LDPE, LLDPE, and HDPE, with and without antioxidants and at different oxygen concentrations in the polymer granules have been studied in extrusion coating processing. The degradation was followed by On Line Rheometry, Size Exclusion Chromatography, Surface Oxidation Index measurements, and GC-MS Chromatography. The degradations starts in the extruder where primary radicals are formed which are subject the auto oxidation when oxygen is present. In the extruder, cross-linking and chain scission reactions are dominating at low and high melt temperatures, respectively, for LDPE, and chain scission is over all dominating for the more linear LLDPE and HDPE resins. Additives such as antioxidants react with primary radicals formed in the melt. Degradation taking place in the film between the die orifice and the quenching point is mainly related to the exposure time to air-oxygen. Melt temperatures above 280°C give a dominating surface oxidation, which increases with the exposure time to air between die orifice and quenching. A number of degradation products were identified, for example, aldehydes and organic acids, which were present in homologous series.

INTRODUCTION

Polyethylene is the most frequently used polymer in packaging. The polyethylene is converted into packaging materials by thermal processes such as film blowing, sheet extrusion, or extrusion coating on substrates such as paperboard. An important prerequisite for food packaging materials is that they should not emit substances that interfere with the product, i.e., cause smell and taste. Because of the high temperatures used in polymer processing degradation occurs [1]. Degradation of polymer molecules is related to thermal stress in combination with mechanical stress during, e.g., processing in an extruder. Smoke released from polyethylene at the extruder die orifice consists of degradation products containing aldehydes, ketones and carboxylic acids[2-9]. Many of these products have very characteristic odours at sub-ppb levels[10], which make them a potential cause to taste and odour.

Based on the knowledge from previous work[9] regarding compounds emitted in the extruder smoke, the aim of the present work was to investigate in which step of the extrusion process the oxidative degradation products are formed during extrusion coating with polyethylene

EXPERIMENTAL

Materials.
One low-density polyethylene, one bi-modal linear low-density polyethylene, and one high-density polyethylene, designed for extrusion coating were selected for this work[11] (Table 1). The LLDPE and the HDPE polymers were produced with the Borstar technology. The LLDPE and HDPE grades contained an antioxidant, Irganox® B 561. The concentration of the antioxidant was 400 ppm. A special LDPE grade (CA 8200 AO) containing the same antioxidant package was prepared through mixing of the LDPE with the antioxidant in a laboratory compounding line. The material was processed twice to secure a uniform antioxidant concentration of 400 ppm. Granulates were used as shipped in PE bags, or after saturation with nitrogen to reduce the amount of oxygen dissolved in the polymer.

Nitrogen saturation

Saturation of PE granulates with N_2 was done batchwise in a stainless steel cylinder, at the bottom closed by a valve, which was connected to a short pipe fitting the extruder inlet section. The cylinder was also equipped with a N_2 inlet close to the top and an outlet tube close to the valve, which at the other end was attached to the pipe fitting the extruder. This arrangement ensured N_2 purge also in the extruder feeding zone. [11]

Process equipment.

On Line Rheometer

Flow properties of the polymer melt were measured by an On Line Rheometer, OLR, Dr. Collin GmbH, connected to a Haake Rheocord 90 extruder (Figure 1). The extruder was equipped with a screw of Φ19 mm, having a length to diameter (L:D) ratio of 24:1, and a compression ratio of 4:1. The screw was fitted with a Maddoc shear module. The OLR concept is based on a gear pump and a set of exchangeable capillaries. The set-up used had three capillaries with circular cross sections (Table 2). [11] Knowing the volume flow Q (m³/s) through a capillary with length l (m) and radius r (m), and a measured pressure drop over the capillary ΔP (Pa), the melt viscosity was calculated according to equations 1-3[12].

$$\text{Shear rate (s}^{-1}) \qquad \dot{\gamma} = \frac{4}{\pi} \frac{Q}{r^3} \qquad\qquad \text{.................... 1}$$

$$\text{Shear stress (Pa)} \qquad \sigma = \frac{\Delta P}{2\left(\dfrac{l}{r}\right)} \qquad\qquad \text{.................... 2}$$

$$\text{Viscosity (Pas)} \qquad \eta = \frac{\sigma}{\dot{\gamma}} = \frac{\pi}{8} \frac{\Delta P}{Q} \frac{r^4}{l} \qquad \text{.................... 3}$$

Plotting viscosity against shear rate according to the Carreau equation[13] (Equation 4) the viscosity at zero shear rate, $\eta_{\gamma=0,}$ was obtained by extrapolation.

$$\eta = \frac{A}{(1+B\gamma)^C} \qquad\qquad \text{.................... 4}$$

The various extrusion temperature profiles used (Table 3) gave polymer melt temperatures at the exit of 260, 280, and 325°C, designated as extrusion process temperatures. The capillary was held constant at 290°C in all measurements.

Film extrusion

Film extrusion was performed with the same laboratory extruder as that used for the OLR measurements. [11] Using vertical extrusion through a coat-hanger die with an orifice width of 150 mm and height of 0.4 mm into a water bath (Figure 2). By adjusting the distance between the die and the water surface the exposure time to atmospheric O_2 for the melt was controlled. The exposure time between the die orifice and the water surface varied between 0.12 and 1.92 s. The various extrusion temperature profiles used (Table 4) gave polymer melt temperatures at the exit of approximately 260, 280, 300, 315, and 325°C, designated as extrusion process temperatures.

Film sampling.

Samples of the films were taken after running the extrusion for at least 45 min allowing equilibration at every new temperature profile before sampling. After a change of the exposure time the process was run for approximately 10 min before sampling.[11]

Surface oxidation.

Measurements of the total oxidation at the various film surfaces were done by Fourier Transform Infrared Spectroscopy, FTIR, Protégé 460 Spectrometer E.S.P., Nicolet Instrument Corporation. The film sample was applied to an Attenuated Total Reflectance (ATR) device, consisting of a ZnSe diamond coated single bounce crystal in a sample holder, and a Single Reflection ATR unit.[11] By the ATR technique the film surface layer of the film was examined. The spectra obtained were then evaluated by calculating the intensity ratio of the C=O stretch at 1720 cm^{-1} over the C-H vibration at 2660 cm^{-1}. This relation is reported as the Surface Oxidation Index. [11] Transmission spectra of film samples were run in transmission mode using the same spectrometer. The oxidation index was calculated from the spectra as above.

Identification of oxidation products.

Identification of oxidation products was done by gas chromatography in combination with mass spectrometry.[11] Volatiles present in film samples were thermally desorbed, and the desorbed compounds were cold trapped in the injection system of the GC to focus the compounds. They were then vaporised by flash heating and separated and detected by gas chromatography – mass spectrometry.

Sample preparation

A narrow piece of the film (10 cm^2) was cut out from a film sample with clean scissors. The film sample was picked from one of the layers situated in the middle of the coil. The weight of the sample was adjusted to 80 mg, and accurately weighed using a balance. The film sample was wound around a glass-rod and put into a desorption glass tube. The tube was then placed in the sample rack of the thermo desorption auto-sampler.

Analysis

The set-up consisted of a thermo desorption unit equipped with a thermo desorption auto sampler from to a Gas Chromatograph HP5890 Series II equipped with Mass Selective Detector MSD 5971 Series was used. The column was HP-1 (crosslinked methyl siloxane) 60 m x 0.32 mm, with 1.0 μm film thickness. Software used was Chemstation G1701AA Version A.03.00 from Agilent Technologies.[11]

Organic acids (acetic acid to dodecanoic acid) were analysed by integrating the ion-chromatograms at m/z=60, except for propanoic acid. Propanoic acid was not included because it does not give rise to the m/z=60 peak as organic acids do.

The aldehydes (butanal to dodecanal) were analysed by integrating the ion-chromatograms at m/z=44.

Alkanes were identified in the ion-chromatograms at m/z=44.

Chromatogram evaluation

To evaluate the GCMC chromatograms the software program Simca-P8, Umetrics, Umeå, Sweden, for Principal Component Analysis, PCA, has been used. [14]

RESULTS AND DISCUSSION

Several researchers, for example Bikiaris, Gugumus, Holmström, and Barabas,[2, 7, 14-17], have investigated and discussed the thermo-oxidative degradation of polyethylene. The commonly agreed mechanism involves formation of alkyl radicals (R*) through cleavage of covalent bonds, followed by reaction with oxygen to form hydroperoxides (ROOH) in a chain reaction, as shown below:

$$RH \rightarrow R* \rightarrow RO_2* \rightarrow ROOH \rightarrow Oxygenated \ products.$$

Decomposition of the hydroperoxides generates oxygenated products. The oxygenated products can be, for example, alcohols, aldehydes, ketones, acids, and esters[2, 5, 7, 15, 17, 18].

On extrusion coating degradation of polyethylene occurs in the extruder barrel as well as in the hot molten film. The extruded film is exposed to the atmospheric oxygen from the exit of the die orifice until reaching the quenching point, i.e., in the air-gap. In the extruder barrel the polymer may degrade due to thermo-mechanical stress, and

oxidise under the influence of oxygen present in the polyethylene melt. At a given temperature the initial degradation depends on the polyethylene used, the screw design, and the throughput.

In the present work degradation of LDPE, LLDPE, and HDPE during film extrusion was studied. The degradation as function of exposure time to oxygen in the air gap was determined as the carbonyl content by FTIR and by the chemical composition of the degradation products present in the film by GCMS techniques. The degradation in the extruder barrel was monitored by measuring the melt viscosity for various type of LDPEs by means of an on-line rheometer (OLR). The temperature of the melt was controlled in the OLR at 290°C throughout the whole investigation. The effect on the viscosity of varying the temperature profiles in the extruder barrel was investigated. Two types of reactions can occur, i.e., chain scission and cross-linking, and there should be a difference between the evaluated polymers in this respect. The highly branched LDPE would form more radicals than the more linear LLDPE and HDPE polymer. This effect can be attributed to a larger number of branching points in LDPE with loosely bound tertiary hydrogens in the polymer molecule. These hydrogens are the targets for radicals formed, e.g., by the auto oxidation[16].

Four different types of granulates were prepared, namely LDPE, LDPE AO (antioxidant added), and the similar nitrogen saturated resins, LDPE N_2, and LDPE AO N_2. The granulates were processed as described above, and the melt viscosity at 290°C measured on-line. In Table 5 it is shown that the zero shear viscosity for LDPE increases on increasing the temperature from 260°C to 300°C, and then decreases again at 325°C. In other work reported by us[11] we have shown that the weight average mole mass increases with the temperature, i.e., $(\overline{M}_w)_{granulate} < (\overline{M}_w)_{260°C} < (\overline{M}_w)_{280°C}$. The polydispersity, $(\overline{M}_w / \overline{M}_n)$, PDI, increases in the same order. At 325°C, however, both $\overline{M}_w$ and PDI drastically decreases. The number average mol mass $(\overline{M}_n)$ decreases in the order $(\overline{M}_n)_{granulate} > (\overline{M}_n)_{260°C} > (\overline{M}_n)_{280°C} > (\overline{M}_n)_{325°C}$, that is, there is a steady increase of low molecular mass material. Other investigators[16, 19, 20] have stated that LDPE is likely to cross-link during extrusion, especially at temperatures below 300°C. The melt flow index for reprocessed polyethylene has been shown to significantly decrease for each pass through the extruder. It can be observed that the zero shear viscosity for LDPE is significantly lower than that of LDPE AO N_2 at all studied temperatures (Table 5). LDPE AO N_2 should be the resin most resistant to degradation, because the low oxygen content prohibits oxidative degradation and the anti oxidant would inactivate the primary radicals formed. By these combined actions only thermo-mechanical degradation would occur resulting in a high zero shear viscosity as compared with the situation in the presence of oxygen, as evidenced by Table 5. The thermo mechanical degradation increases by the temperature increase between 260 and 325°C, which is shown in Table 5 for the LDPE AO N_2. For all temperatures, the zero shear rate viscosity decreases in the order LDPE AO N_2 > LDPE AO > LDPE N_2 > LDPE. This fact is a result of an increased level of oxidative degradation in the non stabilised polymer, which leads to formation of oxidised compounds with chain-lengths shorter that the average. Although the more oxidised material also contains highly branched or cross-linked molecules, the zero shear viscosity is significantly lower.

Comparison of the highly branched LDPE with the more linear LLDPE and HDPE, all saturated with oxygen (Table 5) [11], leads to the conclusion that highly branched materials have an increased degradation leading to cross-linking, and a dominance of chain scission reactions at high temperatures. For the more linear polymers the chain scission reactions are dominating over the whole temperature interval investigated. This could be influenced by the antioxidants present, which is seen by comparing the zero shear rate viscosity versus temperature behaviour for LDPE and LDPE AO respectively (Table 5).

As the hot polymer melt exits from the extruder die it is exposed to oxygen in the air, and surface oxidation starts. The oxidation of the film exiting the die orifice was studied after quenching the melt in a water bath mounted at a variable distance from the orifice as shown in Figure 2. By this method the exposure time to the air oxygen could be varied. The oxidation level of the film surface after different exposure times was then followed through measurement of the oxidation index by ATR-IR analyses. The oxidation index measurements on LDPE, LLDPE, and HDPE, in Figure 3, obtained at various temperatures and air-gaps clearly showed that surface oxidation was of little importance up to 280°C, while at higher temperatures (300-325°C) oxidation became increasingly important. The level of oxidation increased monotonously with the air-gap, or rather the exposure time to oxygen before quenching, as may be anticipated. It was concluded that the results obtained at the shortest air-gap or exposure time was a measure of

the degradation taking place in the extruder barrel, and that following oxidation is a surface related effect, most probably initiated by smaller reactive molecules enriched at the melt / metal interface in the extruder equipment. In the transmission mode IR measurements very little oxidation was detected at all the temperatures and exposure times studied. This finding leads to the conclusion that the antioxidants do not influence the surface oxidation to any large extent.

As previously reported by Andersson et al.[9], a large number of different aldehydes, ketones and carboxylic acids were identified in smoke generated on film extrusion of LDPE in an extrusion coating process. In the present work the volatile oxidized compounds remaining in the films after the extrusion were determined through desorption at elevated temperature, followed by GC-MS analysis. Linear aldehydes C_2 to C_{12} and carboxylic acids C_2 to C_{12} were identified in all film samples.[11] It is obvious from the oxidation data obtained for all polymers and all temperatures investigated that the main part of oxidation of the polyethylene takes place on exposure of the melt to oxygen at the extruder outlet. The amounts of carbonyl compounds found in the films increase almost linearly with the air gap, which is directly proportional to the exposure time. This is clearly evident from Figure 3, which presents the oxidation index as function of the air gap. The MS results indicate that at shorter exposure times and/or lower processing temperatures aldehydes dominate over carboxylic acids. Similarly to the oxidation index (Figure 3) the total amount of volatile compounds (TIC) seems to be dependant on the oxygen contact time, except for the very short air gaps where larger amounts were found. [11] The latter results can be interpreted as a delayed release of degradation products formed in the extruder barrel.
The sum of the ion counts for aldehydes and acid compounds having the same number of carbon atoms were found to increase with exposure time and extrusion temperature. For LDPE the compounds were ordered as C5>C4>C6>C7>>C2, for LLDPE as C5>C6>C4>C7>>C2, for HDPE as C5>C6>C7>C4>>C2 respectively [11]. In earlier work[9] we have shown that the volatiles present in the smoke formed when the PE melt exits the die orifice contains C_2, C_3, and C_4 compounds with the highest amounts found for acetaldehyde, C_2. The small molecules evaporate from the film at a high rate, thus leaving less amounts in the extruded film. On the other hand, long chain radicals will have diffusion restrictions to move to the film surface and react with oxygen. Medium-sized oxidised molecule i.e. for example C_5 - C_8, will thus dominate in the film. Another restriction is the analytical method, which should be increasingly less sensitive to longer and less volatile molecules.

Degradation products present in LDPE films extruded at 300°C and 80 mm air gap from granulate as delivered and granulate saturated with nitrogen for at least 330 hours were compared. The total amounts of volatiles were found to be equal and most of the volatiles were found to be ordinary oxidised compounds such as alcohols, aldehydes, ketones, and carboxylic acids in the C_4-C_{12} range for both types of granulate. However, differences in the product composition between the films extruded were observed. Film obtained from nitrogen saturated granulate contained increased amounts of ketones, alcohols, methyl alkanes, and methylene alkanes, such as 5-methyl-2-hexanone, 2-hexyl-1-octanol, 1,1'-oxybisdecane, 2-methylpentadecane, cyclodecane, octane, undecane, and 5-methyl-6-methylenedodecane. In this case the degradation is mainly of thermo-mechanical origin and cross-link reactions are less frequent. On the other hand the film extruded from granulate saturated with air contained linear alkanes, dimethyl alkanes, trimethyl alkanes, and acetic acid. The oxygen-containing material will also auto oxidise and the higher number of radicals formed in the extruder will increase the probability to form the more branched volatile products, such as acetic acid and 2,2,5-trimethylhexane, 2,3,4-trimethylpentane, 2,3,3-trimethylpentane, 2,3,4-trimethylhexane. This is in line with the idea that oxidative degradation in the extruder is restricted by the lower amount of oxygen present in the nitrogen-saturated material.

The type of degradation products formed depends of both extrusion temperature and dwell time in the air gap, as previously discussed in relation to surface oxidation (Figure 4) The degradation products predominating at short oxygen exposure time, short air gap, are branched alkanes while at longer exposure times and/or higher temperatures oxidised products such as acids, alcohols, ketones and aldehydes are the characteristic ones, as discussed above. In the intermediate region degradation products such as unsaturated hydrocarbons predominate.

The results can be interpreted in the sense that at the longest exposure to oxygen the highest amounts of oxidised components are present, while at the shortest times mainly branched alkanes are present. This is valid independently

of the extrusion temperature, but for example, carboxylic acids would be most easy detected in the films extruded at high air gaps. The extrusion temperature influences the degradation products in a similar way as the exposure times.

The molecular architecture of the polyethylene has an influence on the predominating degradation products. Comparing volatiles from extruded films of LDPE, LLDPE, and HDPE at 280°C with 80 mm air gap gave the results depicted in Figure 5. In the highly branched LDPE aldehydes such as, hexanal, heptanal, pentanal, and octanal were the characteristic volatile degradation products. The most linear polyethylene investigated, HDPE, had unsaturated alcohols and linear alkanes like decane and dodecane as the most characteristic volatiles. The short-chain branched LLDPE, showed branched alkanes as the most typical degradation products for this type of polyethylene. The two linear polyethylenes showed significant peeks of dodecane, tetradecane, and hexadecane in their GCMS chromatograms. There are probably longer alkanes present in the film but they will not be observed due to the used analytical set up. Volatile residuals from degraded antioxidant compounds were detected in the stabilised LLDPE and the HDPE grades.

CONCLUSIONS

It could be concluded from this work that the degradation of polyethylene taking place in the extruder barrel, in addition to thermo mechanical degradation, is dependant on the amount of oxygen present in the melt, and might be controlled by antioxidants, which interact with the formed radicals, and slows down the degradation.

Degradation of the extruded film between the die orifice and the quenching point is related to the exposure time to air-oxygen and is independent of antioxidant being present. The film degradation is a surface related process.

The oxidised compounds present in the extruded films contain aldehydes and carboxylic acids and the composition is shifted towards compounds with shorter carbon chain lengths when exposure time and/or processing temperature are increased. In a previous work regarding smoke emitted at extrusion coating, mostly oxidised C_2-C_4 compounds were found, while in the present work oxidised compounds ranging from C_2 to C_{12} have been identified in the films, with a maximum at C_5. The distribution of chain lengths is related to the ability of the compounds to vaporize from the film surface.

Antioxidants are not very effective in preventing oxidation in the air gap, because most of the aldehydes or acids were formed in this location. Since these compounds may cause off flavour it can be concluded that phenolic antioxidant additives should not be very effective in preventing off taste or odour.

ACKNOWLEDGEMENTS

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TABLES AND FIGURES

Table 1 Polyethylene resins used in the study. The LDPE resin is a high-pressure type produced with a peroxide initiator, and the LLDPE and HDPE resins are bimodal low-pressure grades.

Resin type	Grade	Density (kg/m^3)	Melt flow index [3] (g/10min)	MWD M_w/M_n	Antioxidant[4]
LDPE	CA 8200[1]	920	7.5	25	-
LDPE AO	CA 8200[1]	920	6.5	na.	400 ppm
LLDPE	LE 1000[2]	932	12	14	400 ppm
HDPE	CB 9600[2]	960	9	14	400 ppm

na. equal for not analysed.
1) Autoclave process, Borealis AS, Norway
2) The Borstar process, Borealis OY, Finland
3) 2.16 kg @ 190°C.
4) Irganox B 561

Table 2 On Line Capillary Rheometry, OLR. Capillary dimensions and shear rates used.

Capillary	Length (mm)	Diameter (mm)	Gear pump (rpm)	Shear rate (s^{-1})
1	9.000	0.500	1	896
			25	22409
2	42.187	1.102	1	84
			25	2093
3	45.372	2.090	1	12
			25	307

Table 3 Temperature profiles for the Haake extruder and the Collin On Line Rheometer. The extruder screw speed was held constant at 100 rpm throughout the whole test.

Extrusion temperature (°C)	Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Capillary (°C)
260	220	240	260	290
280	230	250	280	290
325	240	285	325	290

Table 4 Extruder temperature settings used, to achieve polymer melt temperatures of 260, 280, 300, 315, and 325°C. Zone 1-3 represents the extruder barrel, zone 4 the adapter and zones 5 and 6 the die.

	Melt temperature (°C)				
	260	**280**	**300**	**315**	**325**
Zone 1 (°C)	220	225	230	235	237
Zone 2 (°C)	240	255	270	285	290
Zone 3 (°C)	260	280	300	315	325
Zone 4 (°C)	260	280	300	315	325
Zone 5 (°C)	258	275	290	305	315
Zone 6 (°C)	258	275	290	305	315

Table 5 Melt viscosity at 290°C and zero shear rate for LDPE, LLDPE, and HDPE, extrusion process temperature 260, 280, and 325°C. The viscosity at zero shear rate ($\eta_{\gamma=0}$) reported is the mean value of the number of runs (n) reported, σ represents the standard deviation. [11]

	Zero shear viscosity at 290°C (Pas)								
EPT[1] °C	**260**			**280**			**325**		
	$\eta_{\gamma=0}$	σ	ν	$\eta_{\gamma=0}$	σ	ν	$\eta_{\gamma=0}$	σ	ν
LDPE	181	2	6	185	2	6	172	3	6
LDPE N$_2$[2]	187	4	7	185	2	7	179	4	7
LDPE AO[3]	193	2	7	195	3	6	182	4	6
LDPE AO N$_2$[4]	205	3	6	203	6	7	189	6	6

[1] Extrusion Processing Temperature EPT
[2] N$_2$ saturated granules
[3] Anti Oxidant
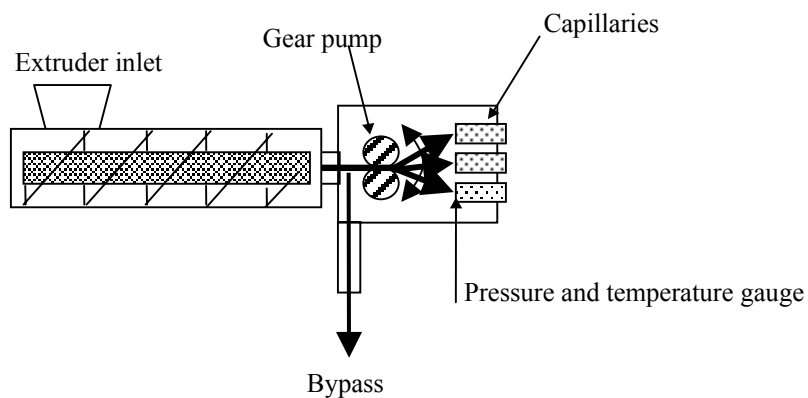[4] Anti Oxidant and N$_2$ saturated granules
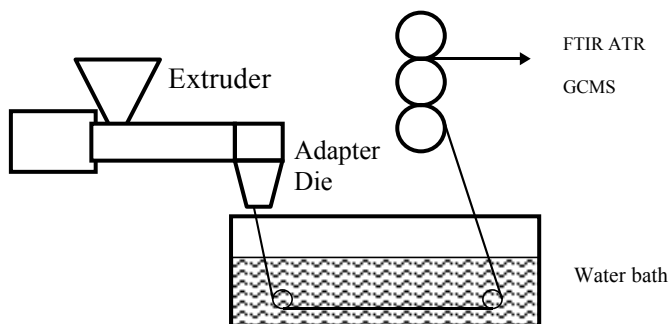
Figure 1 The On Line Rheometer set-up.

Figure 2
Film extrusion set-up. The exposure to air (oxygen) was adjusted by changing the water level in the bath. The exposure distance was 5 - 80 mm.
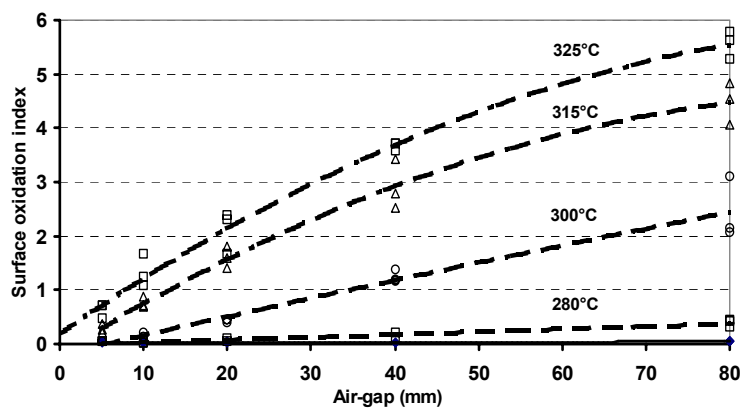

Figure 3 Surface oxidation index for LDPE, LLDPE and HDPE as function of air-gap, for different extrusion process temperatures 260, 280, 300, 315, and 325°C. The different polyethylenes behaved similarly and are reported with the same symbols in the plot.
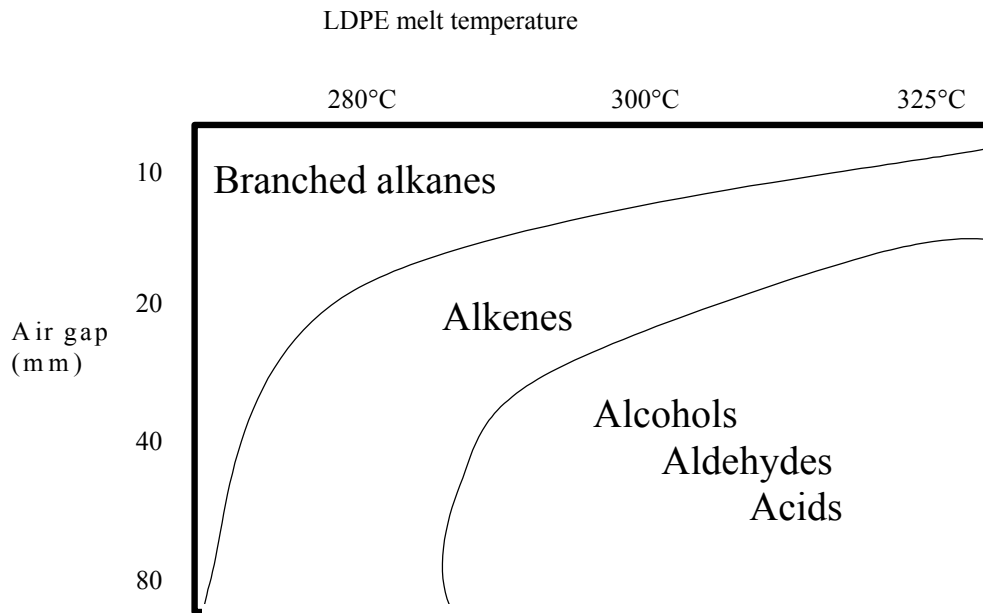
LDPE melt temperature

| | 280°C | 300°C | 325°C |

10   Branched alkanes

Air gap
(mm)

20   Alkenes

Alcohols
40   Aldehydes
      Acids

80

Figure 4 Degradation products as function of extrusion process conditions for LDPE.

LLDPE

HDPE   Anti oxidant residuals
        Dodecane   Branched alkanes

Decane
Alkenes   Alcohols
Unsaturated alcohol   Pentanal
                       Acids

          Octanal
                    Heptanal   LDPE
                    Hexanal
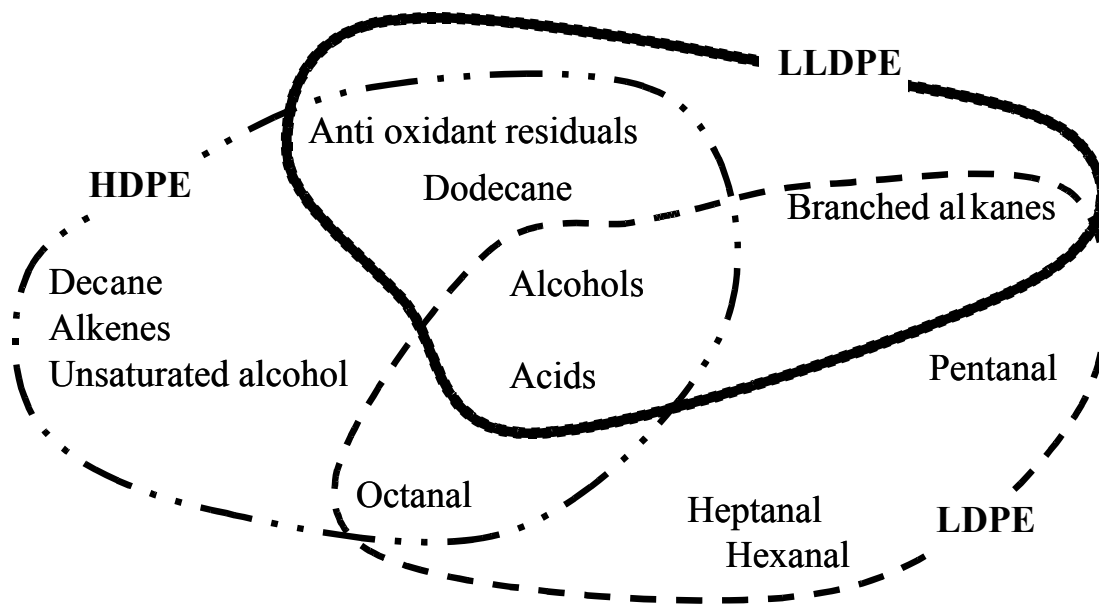
Figure 5 Typical degradation products for extruded LDPE, LLDPE, and HDPE films at 280°C melt temperature and 80mm air-gap.

Degradation of
LDPE – LLDPE – HDPE
in film extrusion

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Objectives

- Where does degradation occur?

- What are the degradation products?

We investigated

- On line rheometry
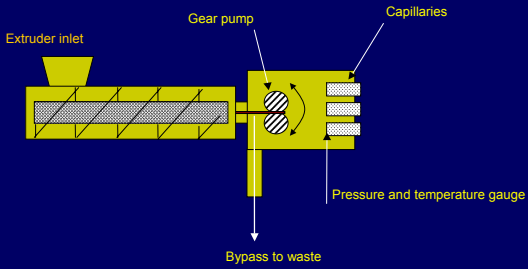
- Surface oxidation

- Degradation products

Polymer Grades Investigated

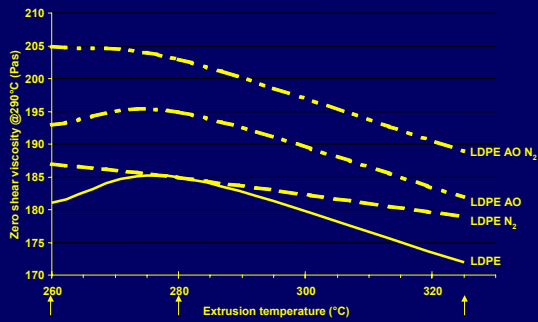| Polymer	Borealis grade	Antioxidant	Origin
LDPE	CA 8200	-	Autoclave
LDPE AO	CA 8200	400 ppm	Autoclave
LLDPE	LE 1000	400 ppm	Borstar
HDPE	CB 9600	400 ppm	Borstar

On Line Rheometry

- Viscosity as f (extrusion temperature)
  260, 280, and 325°C
- Viscosity as f (stabilisation)
  LDPE, LDPE + antioxidant
- Viscosity as f (oxygen content in granulate)
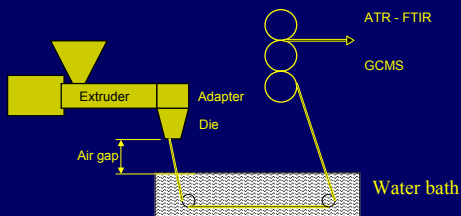 Air and Nitrogen saturated granulates

On Line Rheometer, OLR

Extruder inlet

Gear pump

Capillaries

Pressure and temperature gauge

Bypass to waste

Zero Shear Viscosity @ 290°C as f(oxygen, antioxidant and temperature)

Zero shear viscosity @290°C (Pas)

210
205
200
195
190
185
180
175
170

260   280   300   320

Extrusion temperature (°C)

LDPE AO N$_2$

LDPE AO

LDPE N$_2$

LDPE

Film Extrusion

ATR - FTIR
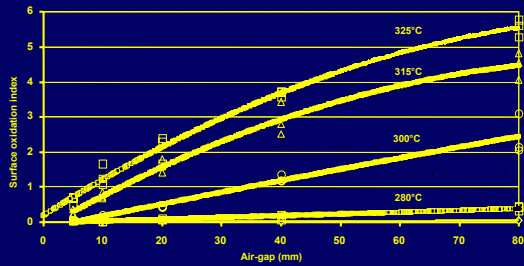
GCMS

Extruder

Adapter

Die

Air gap

Water bath

Surface Oxidation
Carbonyl content as
f (temperature, air gap, and polymer)

Degradation Products

- Degradation products as
  - f (oxygen content in granulate)
  - f (air gap, extrusion temperature)
  - f (polymer)

Degradation Products in LDPE as $f(O_2$ cont.)

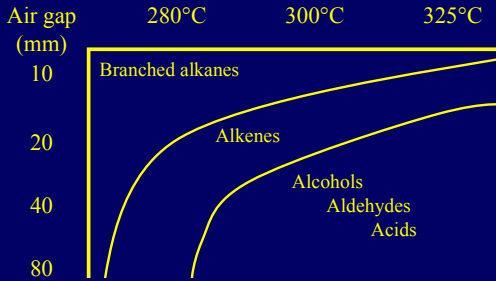| Nitrogen saturated granulate	Air saturated granulate
Alkenes	Alkanes
Methyl alkanes	Dimethyl alkanes
Methylene alkanes	Trimethyl alkanes
	Acetic acid

LDPE Degradation Products
as f(air gap, extrusion temperature)

Air gap (mm)	280°C	300°C	325°C

Branched alkanes

Alkenes

Alcohols
Aldehydes
Acids

10
20
40
80

Typical Degradation Products
@280°C f(polymer) at 80mm air-gap

LLDPE

HDPE

Antioxidant residuals
Dodecane

Branched alkanes

Decane
Alkenes
Unsaturated alcohol

Alcohols

Acids

Pentanal

Octanal

Heptanal
Hexanal

LDPE
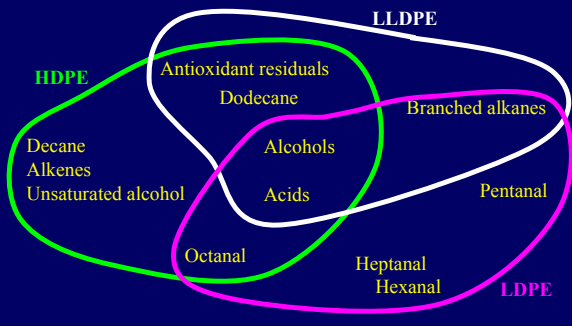
Conclusions

- Degradation is initiated in the extruder
- Oxidative degradation in the air gap.
- Oxidative degradation is a surface phenomenon
  - depends on time in air gap
  - polyethylene type of no significance.
- Antioxidants do not prevent surface oxidation.

Thank you for your attention