

# Degradation of Polyethylene During Extrusion. II. Degradation of Low-Density Polyethylene, Linear Low-Density Polyethylene, and High-Density Polyethylene in Film Extrusion

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**ABSTRACT:** The degradation of different polyethylenes—low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE)—with and without antioxidants and at different oxygen concentrations in the polymer granulates, have been studied in extrusion coating processing. The degradation was followed by online rheometry, size exclusion chromatography, surface oxidation index measurements, and gas chromatography–mass spectrometry. The degradations start in the extruder where primary radicals are formed, which are subject to the auto-oxidation when oxygen is present. In the extruder, crosslinking or chain scissions reactions are dominating at low and high melt temperatures, respectively, for LDPE, and chain scission is overall 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 too. A number of degradation products were identified—for example, aldehydes and organic acids—which were present in homologous series. The total amount of aldehydes and acids for each number of chain carbon atoms were appeared in the order of C5>C4>C6>C7>C2 for LDPE, C5>C6>C4>C7>C2 for LLDPE, and C5>C6>C7>C4>C2 for HDPE. The total amounts of oxidized compounds presented in the films were related to the processing conditions. Polymer melts exposed to oxygen at the highest temperatures and longest times showed the presence dialdehydes, in addition to the aldehydes and acids. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1525–1537, 2004

**Key words:** polyethylene; extrusion; degradation products; antioxidants; oxidation

## 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 tempera-

tures used in polymer processing, degradation occurs.<sup>1</sup> 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.<sup>2–9</sup> Many of these products have very characteristic odors at sub-ppb levels,<sup>10</sup> which make them a potential cause to taste and odor.

Based on the knowledge from previous work<sup>9</sup> 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. It is believed that exposure to air of the polymer melt is more important to degradation than the extrusion process itself. The present investigation focused on melt viscosity changes during the film extrusion of PE, and on the presence of oxidized degradation products in the extruded material, i.e., aldehydes and carboxylic acids, which may cause

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TABLE I  
Polyethylene Resins Used in the Study

Resin type	Grade	Density (kg/m <sup>3</sup> )	Melt flow index <sup>a</sup> (g/10 min)	MWD $M_w/M_n$	Type of branching <sup>b</sup>	Antioxidant <sup>c</sup>
LDPE	CA 8200	920	7.5	25	SCB and LCB	None
LDPE	CA 8200 AO	920	6.5	na	SCB and LCB	Yes
LLDPE	LE 1000	932	12	14	SCB	Yes
HDPE	CB 9600	960	9	14	SCB	Yes

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

na: not analyzed.

<sup>a</sup> 2.16 kg @ 190°C.

<sup>b</sup> SCB: short chain branching; LCB: long chain branching.

<sup>c</sup> Irganox B 561, 400 ppm.

off-flavor in the packed product. The degradation products were determined semiquantitatively.

## EXPERIMENTAL

### Materials

One low-density polyethylene (LDPE, CA 8200, Borealis AS, Stathelle, Norway), one bimodal linear low-density polyethylene (LLDPE, LE 1000, Borealis OY, Finland), and one high-density polyethylene (HDPE, CB 9600, Borealis OY, Finland) designed for extrusion coating were selected for this work (Table I). The LLDPE and the HDPE polymer were produced with the Borstar technology. The LLDPE and HDPE grades contained an antioxidant, Irganox<sup>®</sup> B 561 from Ciba Specialty Chemicals, Basel, Switzerland. The concentration of Irganox<sup>®</sup> B 561 was 400 ppm. Irganox<sup>®</sup> B 561 is a mix of different antioxidants consisting of 20% Irganox<sup>®</sup> 1010 and 80% Irgafos<sup>®</sup> 168. A special LDPE grade (CA 8200 AO) containing the same antioxidant package was provided by Borealis AS, Norway, through mixing of CA 8200 with Irganox<sup>®</sup> B 561 at 200°C in a laboratory 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<sub>2</sub> was done batchwise in a stainless steel cylinder, at one end closed by a welded stainless steel plate and at the other by a welded valve, which was connected to a short pipe fitting the extruder inlet section (Fig. 1). The cylinder was also equipped with a N<sub>2</sub> inlet close to the welded plate 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<sub>2</sub> purge also in the extruder feed-

ing zone. A batch of 4300 g of PE pellets in the 7.0 dm<sup>3</sup> chamber gave a free gas volume of approximately 2.7 dm<sup>3</sup>. N<sub>2</sub> (Air Liquide, Malmö, Sweden) was fed to the device at room temperature and at approximately 0.1 MPa, giving a gas flow of 20 mL/min, and passed through the device for at least 14 days, corresponding to more than 150 volume changes. After the treatment the effluent gas had an O<sub>2</sub> content below the detection limit of 5 ppb Oxygen at 23°C for an Oxtran 2/20 (Mocom Instruments, Minneapolis, MN).

### Process equipment

#### Online rheometer

Flow properties of the polymer melt were measured by an Online rheometer (OLR, Dr. Collin GmbH, Mu-

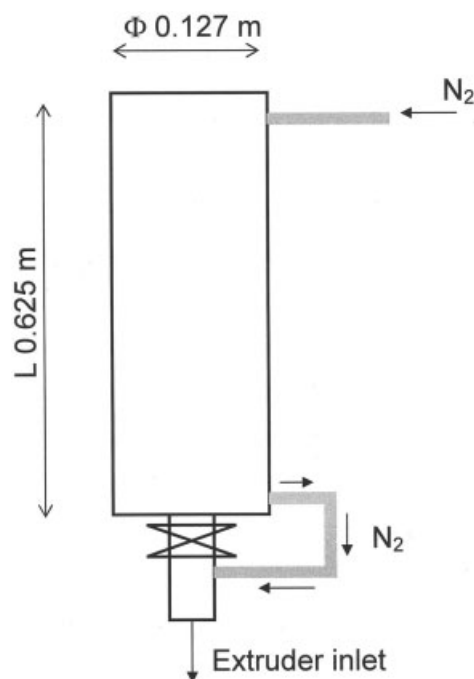
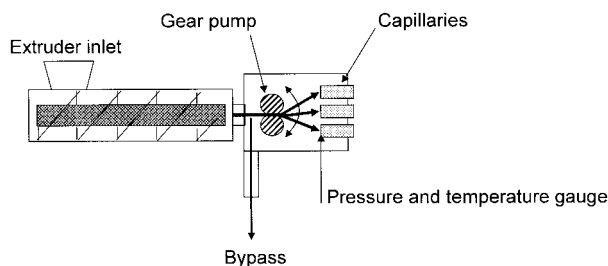


Figure 1 Equipment used for nitrogen saturation.

**TABLE II**  
**Online Capillary Rheometry: Capillary Dimensions and Shear Rates Used**

Capillary	Length (mm)	Diameter (mm)	Gear pump (rpm)	Shear rate (s <sup>-1</sup> )
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

nich, Germany) connected to a Rheocord 90 extruder (HAAKE, Karlsruhe, Germany). The extruder was equipped with a screw of  $\Phi 19$  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 Madoc shear module. The OLR concept is based on a gear pump and a set of exchangeable capillaries. The setup used had three capillaries with circular cross sections (Table II). The gear pump ensured constant and well-defined volume flow through the capillaries. The capillaries discharged directly into surrounding atmosphere. A pressure gauge and a thermocouple were installed at the capillary inlets for monitoring melt pressure and temperature. A selector valve directed the polymer melt to one capillary at the time (Fig. 2). A measuring sequence consisted of the following steps; starting with one capillary and the gear pump at low speed (1 rpm), 60 s equilibration time, and then measuring melt pressure and temperature during 10 s. The gear pump was then switched to high speed (25 rpm), and equilibration and measuring melt pressure and temperature were done as above. The polymer flow was then redirected to the next capillary. Measuring was again started at low speed, and the measuring sequence repeated. This procedure was repeated for all three capillaries. Three different process temperature profiles were used in the extruder, corresponding to polymer melt temperatures in the extruder front zone of 260, 280, and 325°C (Table III). A constant screw speed (100 rpm) was used ensuring that an excess of molten polymer was delivered to the gear pump. A by-pass


**Figure 2** The OLR setup.

**TABLE III**  
**Temperature Profiles for the Haake Extruder and the Collin Online Rheometer**

Extrusion temperature (°C)	Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Capillary (°C)
260	220	240	260	290
280	230	250	280	290
300	240	270	300	300
325	240	285	325	290

The extruder screw speed was held constant at 100 rpm throughout the whole test.

tube released the excess of polymer supplied from the extruder. The gear pump, and the capillaries were kept at 290°C during all measurements. The OTR equipment, gear pump and capillaries were temperature controlled within  $\pm 1^\circ\text{C}$  by electrical heaters and thermocouples in the melt. A second test series was made at a polymer melt temperature of 300°C with all other parameters as above (Table III). Each PE grade was measured at the various extruder temperature settings, and then purged with the next PE grade. At each change of extruder temperature setting, 35 min equilibration time was allowed before starting the measuring sequence. Between each change of polymer grade, an additional 45 min purging time was allowed to ensure that the extruder was well purged from the previous material, and that stable extrusion conditions were reached. Six measurement cycles were performed for each polymer grade and temperature setting.

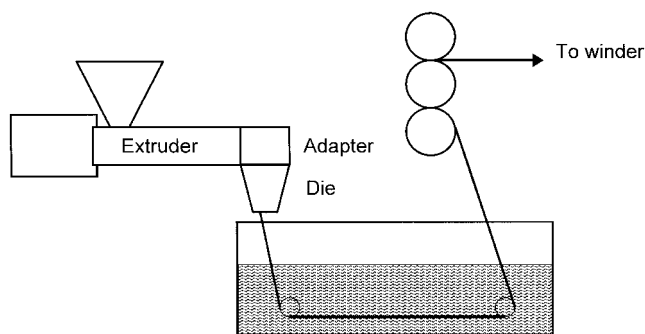
For practical reasons it was preferred to put the pressure gauge in front of the capillary inlet instead of having it in the capillary. The pressure drop over the capillary was approximated to the pressure before the capillary. The viscosity of the melt at different shear rates was calculated from the pressure drop. Knowing the volume flow  $Q$  (m<sup>3</sup>/s) through a capillary with length  $l$  (m) and radius  $r$  (m), and a measured pressure drop over the capillary  $\Delta P$  (Pa), the melt viscosity was calculated according to eqs. (1)–(3).<sup>11</sup>

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

$$\text{Shear stress (Pa)} \sigma = \frac{\Delta P}{2 \left(\frac{\lambda}{r}\right)} \quad (2)$$

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

Plotting viscosity against shear rate according to the Carreau equation<sup>12</sup> [eq. (4)], the viscosity at zero shear rate,  $\eta_{\gamma=0}$  was obtained by extrapolation.



**Figure 3** Film extrusion setup. The exposure to air (oxygen) was adjusted by changing the water level in the bath. The exposure distance was 5–80 mm.

$$\eta = \frac{A}{(1 + B\gamma)^c} \quad (4)$$

#### Film extrusion

Film extrusion was performed with the same laboratory extruder as that used for the OLR measurements. The experimental setup was vertical extrusion made through a coat-hanger die with an orifice width of 150 mm and height of 0.4 mm into a water bath (Fig. 3). By adjusting the distance between the die and the water surface, the exposure time to atmospheric O<sub>2</sub> for the melt was controlled. Increasing the distance between the orifice and the water level increased the exposure time. The distances used were 5, 10, 20, 40, and 80 mm. The maximum distance of 80 mm was a consequence of the melt strength and neck in behavior of the extrudates. The take-off unit was set at a constant speed of 5.0 m/min, and the extruder screw was set at 80 rpm. The various extrusion temperature profiles used (Table IV) gave polymer melt temperatures at the exit of approximately 260, 280, 300, 315, and 325°C, designated as extrusion process temperatures. The residence time for the film in the water bath varied between 6 and 7 s. The exposure time between the die orifice and the water surface varied between 0.12 and 1.92 s.

#### 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.

Sampling of the film was done in two ways. For measuring surface oxidation and identification of degradation products approximately 2 m of the film were cut out and placed as a loose coil wrapped in a grease-free aluminium foil (18 μm, Plus Pack AS, Odense, Denmark). This procedure should protect the sample

from contamination and limit evaporation of low molecular mass material. For molecular mass distribution analysis the samples was cut from films winded to a roll. Samples from each run were reeled individually at separate rolls.

#### 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, Madison, WI, USA). 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 (Di-Comp Probe, ASI Applied Systems, Annapolis, MD, USA). 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<sup>-1</sup> over the C—H vibration at 2660 cm<sup>-1</sup>. This relation is reported as the Surface Oxidation Index. The C=O stretch intensity was taken as the peak height at 1720 cm<sup>-1</sup> using a horizontal base line between 1670 cm and 1770 cm<sup>-1</sup>. The intensity for the C—H vibration was taken as the peak height at 2660 cm<sup>-1</sup> and a horizontal base line at 2400 and 2450 cm<sup>-1</sup>.

Transmission spectra of film samples were run in transmission mode using the same spectrometer. The oxidation index was calculated from the spectra as above.

#### Molecular mass distribution

The molecular mass distribution for the different polymers was analyzed by size exclusion chromatography (SEC, Waters 150CV). The unit was equipped with refractive index and viscosity detectors (Waters Associates, Milford, MA, USA). A set of three HT6E Styragel columns from Waters was used with Trichlorobenzene as eluent at 140°C. Calibration was performed

**TABLE IV**  
Extruder Temperature Settings Used, to Achieve Polymer Melt Temperatures of 260, 280, 300, 315, and 325°C.

	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

Zones 1–3 represents the extruder barrel, zone 4 the adapter, and zones 5 and 6 the die.

with narrow MWD polystyrene standards. The software used was the "Millennium" from Waters Associates.

### Identification of oxidation products

Identification of oxidation products was done by gas chromatography (GC) in combination with mass spectrometry. 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 GC—mass spectrometry (MS).

### Sample preparation

A narrow piece of the film (10 cm<sup>2</sup>) 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 Mettler AT 250 (Mettler Toledo, Greifensee, Switzerland) 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 thermodesorption autosampler.

### Analysis

The setup consisted of a thermodesorption unit (TDS-2) equipped with a thermodesorption autosampler (TDS-A) from Gerstel (Gerstel GmbH & Co. KG, Mülheim an der Ruhr, Germany). Through the desorption chamber a flow of 50 mL/min of He was passed. After equilibration at 20°C the sample tube (Gerstel, OD 6.0 mm/ID 3.9 mm, length 178 mm), was inserted. The temperature was held at 20°C for one minute for flushing the system free from oxygen before increasing the temperature to 100°C at 60°C/min. The temperature was then held at 100°C for 20 min. The flow from the thermo desorption unit was passed through a deactivated capillary transfer line (OD 0.70 mm/ID 0.53 mm and length 145 mm), held at 275°C, to the cooled injection system (CIS-3, Gerstel) in the gas chromatograph. During desorption the He flow (50 mL/min) thorough the desorption chamber passed the cooled injection system, which was held at -70°C to trap the desorbed compounds. After the desorption step the injector was put in splitless position for 1 min. The flow through the injector and the column was then approximately 1 mL/min. The temperature was initially kept at -70°C for 0.5 min and then rapidly increased to 300°C at 12°C/s. The temperature was then held at 300°C for 10 min for cleaning the injector.

A Gas Chromatograph HP5890 Series II (Hewlett Packard, Palo Alto, CA, USA) equipped with Mass Selective Detector MSD 5971 Series from Agilent Technologies (Agilent Technologies, Palo Alto, CA, USA) was used. The column was HP-1 (crosslinked methyl siloxane) 60 m × 0.32 mm, with 1.0 μm film thickness. The flow was pressure regulated with a head pressure of 9 psi, which gave a column flow of 1.0 to 1.5 mL/min. The oven temperature was initially held at 20°C for 0.5 min and then increased to 260°C at 5°C/min. The temperature was held at 260°C for 4 min. The transfer line to the mass selective detector was kept at 280°C. Electron impact mode was used at 70 eV. The scanning was performed between *m/z* 30 and 350. The resulting electron multiplication voltage was used in the standard spectra autotuning mode. Solvent delay was 5 min. Software used was Chemstation G1701AA Version A.03.00 from Agilent Technologies.

Organic acids (acetic acid to dodecanoic acid) were analyzed 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 analyzed by integrating the ion chromatograms at *m/z*=44.

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

## RESULTS AND DISCUSSION

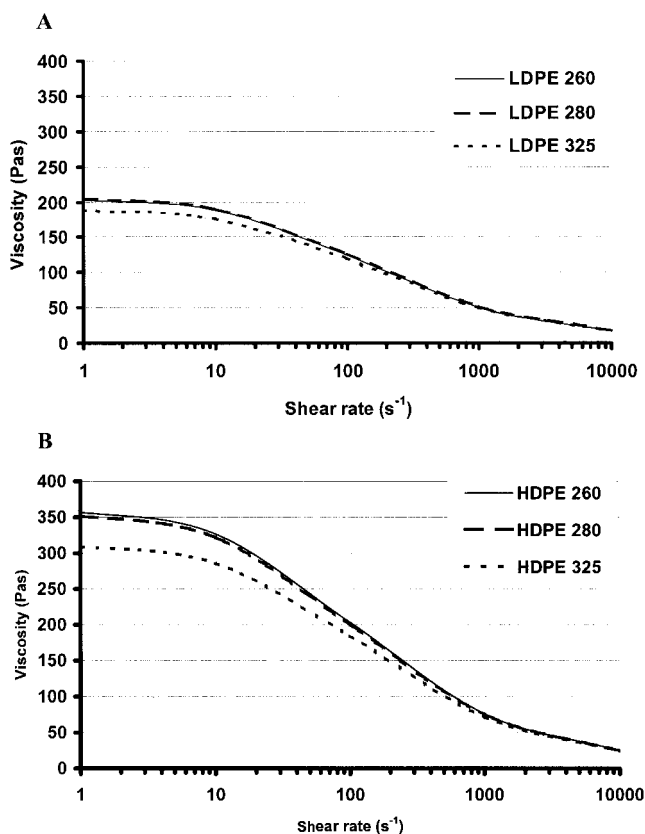
Several researchers—for example, Bikiaris, Gugumus, Holmström, and Barabas,<sup>2,7,14–17</sup>—have investigated and discussed the thermo-oxidative degradation of polyethylene. The commonly agreed mechanism involves formation of alkyl radicals (R<sup>\*</sup>) through cleavage of covalent bonds, followed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



Oxygenated products

Decomposition of the hydroperoxides generates oxygenated products. The oxygenated products can be, for example, alcohols, aldehydes, ketones, acids, and esters.<sup>2,5,7,14–17</sup>

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 thermomechanical stress, and oxidize under the influence of oxygen present in the polyethylene melt. At a given temperature, the initial degradation depends on the



**Figure 4** Melt viscosity at 290°C at different shear rates for (A) LDPE and (B) HDPE, extruded at 260, 280, and 325°C.

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 in the extruder barrel was monitored by measuring the melt viscosity for the various polymers by means of an 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 crosslinking, 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.<sup>15</sup>

In Figure 4 curves representing the melt viscosity at 290°C as a function of shear rate are shown for both LDPE and HDPE. The curves were obtained at extrusion temperatures of 260, 280, and 325°C, respectively (Table III). The melt viscosity clearly decreased with increasing process temperature, which indicates that

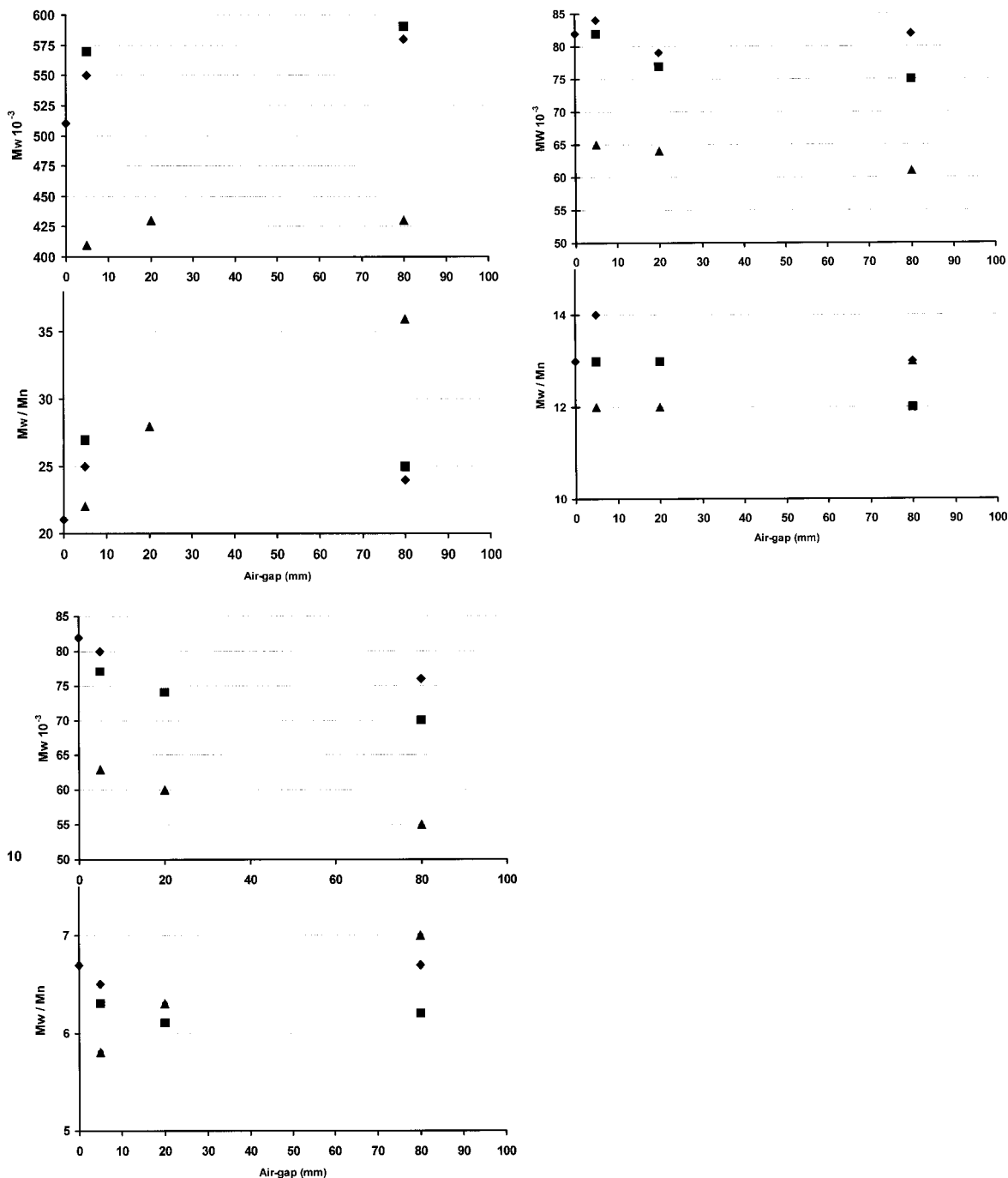
chain scission dominates over crosslinking, especially at the highest temperatures.

In the lower temperature region, i.e., at 260–280°C, a small but reproducible increase in viscosity with temperature was observed for LDPE, indicating a slight predominance for crosslinking. For HDPE, however, a small decrease in viscosity was observed. These observations were corroborated by measurement of molecular mass averages, ( $\bar{M}_w$ ), and polydispersity, ( $\bar{M}_w/\bar{M}_n$ ), for virgin material, and for material that was obtained directly after the die, i.e., at an air gap of 5 mm (Fig. 5). For LDPE both  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  values were higher at a processing temperature of 280°C compared with the values obtained at 260°C, and also substantially higher than those measured for virgin material, as shown in Figure 5(a).

For LLDPE,  $\bar{M}_w$  decreased monotonously from the virgin material over 260 and 280 to 325°C, as seen in the Figure 5(b). For HDPE a similar behaviour as for LLDPE was observed [Fig. 5(c)]. This observation and the fact that the polydispersity index decreased indicates that chain scission dominates over crosslinking reactions for these polymers. At 325°C all types of polyethylene materials clearly showed lower  $\bar{M}_w$  values than were observed after extrusion at lower temperatures, which shows that a substantial degradation of the polymers through chain scission has occurred. These conclusions are based on the assumption that at the shortest air gap (5 mm), degradation due to exposure to atmospheric oxygen should be of minor importance as compared to the degradation taking place in the extruder barrel.

As discussed above, oxidative attack on the polymer by oxygen entrapped in the polymer melt may be one cause to degradation in the extruder barrel. To investigate this idea, the small amount of oxygen present in polymer pellets stored at normal atmosphere was displaced by nitrogen, and the whole extrusion process was performed under a nitrogen blanket. In Figure 6 the results from OLR measurements at 290°C and at a processing temperature of 300°C (Table III) are shown for both LDPE and HDPE granulates saturated with nitrogen and air, respectively. Nitrogen-saturated LDPE granulate suffered a clear drop in viscosity compared with the air-saturated one, which can be interpreted as chain scission dominating over crosslinking. Nitrogen-saturated HDPE gave similar results, but the effect was smaller. In the absence of oxygen the radical concentration in the melt should be lower and, consequently, radical coupling should be less frequent than in the presence of oxygen. It has to be taken into account that the HDPE resin used in the experiments contained a standard phenolic antioxidant while the LDPE did not. The observed differences between LDPE and HDPE may thus depend on this fact.

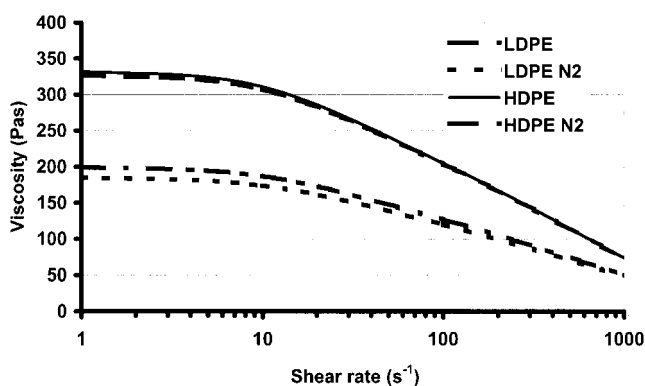
It was not possible to obtain the HDPE without any antioxidant added, and for comparison the behavior



**Figure 5A** Figure 5A Molecular mass ( $\bar{M}_w$ ) and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) for LDPE as a function of exposure time, air gap, and extrusion process temperature ( $\blacklozenge$  260,  $\blacksquare$  280, and  $\blacktriangle$  325°C). The value at 0 min air gap represents the starting material. **Figure 5B** Molecular mass ( $\bar{M}_w$ ) and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) for LLDPE as a function of exposure time, air gap, and extrusion process temperature ( $\blacklozenge$  260,  $\blacksquare$  280, and  $\blacktriangle$  325°C). The value at 0 min air gap represents the starting material. **Figure 5C** Molecular mass ( $\bar{M}_w$ ) and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) for HDPE as a function of exposure time, air gap, and extrusion process temperature ( $\blacklozenge$  260,  $\blacksquare$  280, and  $\blacktriangle$  325°C). The value at 0 min air gap represents the starting material.

of LDPE in the presence of the same antioxidant package as that used for HDPE was studied. Four different types of granulates were prepared, namely LDPE, LDPE AO (antioxidant added), and the similar nitrogen saturated resins, LDPE N<sub>2</sub>, and LDPE AO N<sub>2</sub>. The granulates were processed as described above, and the

melt viscosity at 290°C measured online. In Table V it is shown that the zero shear viscosity for LDPE increases on increasing the temperature from 260 to 300°C, and then decreases again at 325°C. Figure 5(a) shows that the molecular mass increases with the temperature, i.e.,  $(\bar{M}_w)_{\text{granulate}} < (\bar{M}_w)_{260^\circ\text{C}} < (\bar{M}_w)_{280^\circ\text{C}}$ .



**Figure 6** Melt viscosity at 300°C for LDPE and HDPE saturated with nitrogen and normal air. Extrusion process temperature 300°C.

The polydispersity (PDI) increases in the same order. At 325°C, however, both  $\bar{M}_w$  and PDI drastically decreases. The number average molar mass ( $\bar{M}_n$ ) as calculated from Figure 5 decreases in the order  $(\bar{M}_n)_{\text{granulate}} > (\bar{M}_n)_{260^\circ\text{C}} > (\bar{M}_n)_{280^\circ\text{C}} > (\bar{M}_n)_{325^\circ\text{C}}$ , that is, there is a steady increase of low molecular mass material. For the LDPE it can be assumed that both oxidative and thermo mechanical degradation takes place, with the formation of a high number of degraded molecules, which decreases  $\bar{M}_n$  and produces a large number of radicals. The high concentration of radicals increases the probability for two large radicals to meet and terminate, creating large, highly branched molecules, which would tend to increase  $\bar{M}_n$ . Other investigators<sup>15,18,19</sup> stated that LDPE is likely to crosslink 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 significant lower than that of LDPE AO N<sub>2</sub> at all studied temperatures (Table V). LDPE AO N<sub>2</sub> should be the resin most resistant to degradation, because the low oxygen content prohibits oxidative degradation and the antioxidant would inactivate the primary radicals formed. By these combined actions only thermomechanical degradation would occur resulting in a high zero shear viscosity as compared with the situation in the presence of oxygen, as evidenced by Table V.

The thermomechanical degradation increases by the temperature increase between 260 and 325°C, which is shown in Table v for the LDPE AO N<sub>2</sub>. For all temperatures, the zero shear rate viscosity decreases in the order LDPE AO N<sub>2</sub> > LDPE AO > LDPE N<sub>2</sub> > LDPE. This fact is a result of an increased level of oxidative degradation, which leads to formation of oxidised compounds with chain lengths shorter than the average. Although the more oxidised material also contains highly branched or crosslinked material, the zero shear viscosity is significantly lower.

On comparison of the highly branched LDPE with the more linear LLDPE and HDPE all saturated with oxygen (Table V), leads to the conclusion that highly branched materials have an increased degradation leading to crosslinking and at high temperature chain scission reactions dominate. For the more linear polymers, the chain scission reactions are dominating in the whole temperature interval investigated. This could be influenced by the antioxidants present comparing the zero shear rate viscosity temperature behaviour for LDPE respectively LDPE AO (Table V).

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

**TABLE V**  
Melt Viscosity at 290°C and Zero Shear Rate for LDPE, LLDPE, and HDPE, Extrusion Process Temperature 260, 280, 300, and 325°C

	Zero shear viscosity at 290°C (Pas)											
	260 EPT <sup>a</sup> (°C)			280 EPT (°C)			300 EPT (°C)			325 EPT (°C)		
	$\eta_{\gamma=0}$	$\sigma$	<i>n</i>	$\eta_{\gamma=0}$	$\sigma$	<i>n</i>	$\eta_{\gamma=0}$	$\sigma$	<i>n</i>	$\eta_{\gamma=0}$	$\sigma$	<i>n</i>
LDPE	181	2	6	185	2	6	199	3	3	172	3	6
LDPE N <sub>2</sub> <sup>b</sup>	187	4	7	185	2	7	185	4	4	179	4	7
LDPE AO <sup>c</sup>	193	2	7	195	3	6				182	4	6
LDPE AO N <sub>2</sub> <sup>d</sup>	205	3	6	203	6	7				189	6	6
LLDPE	251	3	7	249	2	6				216	3	7
HDPE	340	7	7	334	5	6	321	4	3	291	5	7
HDPE N <sub>2</sub> <sup>2)</sup>							327	5	4			

The viscosity at zero shear rate ( $\eta_{\gamma=0}$ ) reported is the mean value of the number of runs (*n*) reported,  $\sigma$  represents the standard deviation.

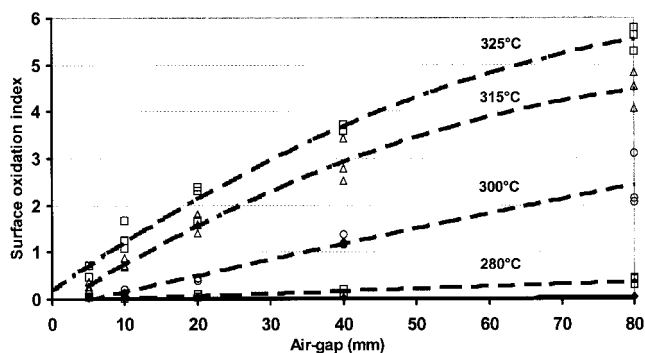
<sup>a</sup> EPT: extrusion processing temperature.

<sup>b</sup> N<sub>2</sub> saturated granules.

<sup>c</sup> Antioxidant Irganox B561, 400 ppm.

<sup>d</sup> Antioxidant Irganox B561, 400 ppm, and N<sub>2</sub> saturated granules.





**Figure 7** Surface oxidation index for LDPE, LLDPE, and HDPE as a 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.

bath mounted at a variable distance from the orifice as shown in Figure 7. 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 attenuated total reflectance-infrared analyses. The oxidation index measurements on LDPE, LLDPE, and HDPE in Figure 7 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 showed very little oxidation at all temperatures and exposure times. This leads to the conclusion that the antioxidants do not influence the surface oxidation.

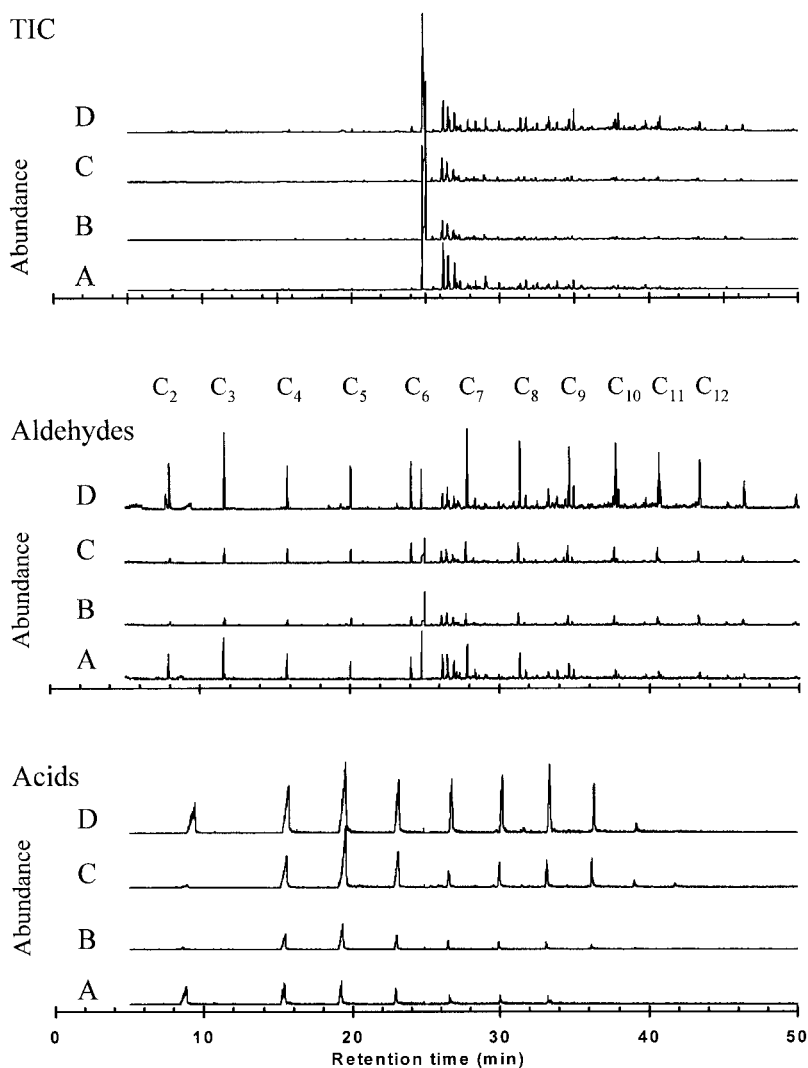
The molecular masses were determined for the extruded materials at various oxygen exposure times. As already discussed, high temperatures in the extrusion process generate a substantial degradation in the extruder barrel for all the materials, as shown in Figure 5. It was observed, however, that there was little correlation between the exposure time to oxygen and the molecular size determined by SEC. It can be concluded that the molecular size measurements reflect the situation in the polymer bulk, which only to a minor degree should be influenced by the surface-localized oxidative degradation.

LLDPE [Figure 5(b)] and HDPE [Figure 5(c)], which both contained antioxidants, showed an increased

degradation with increasing temperature, with only a minor dependence on the exposure time to oxygen. For these polymers, chain transfer of primary radicals to the phenolic antioxidant should limit recombination of large polymer radicals and rather produce polymer chains of lower than average size.

As previously reported by Andersson et al.,<sup>9</sup> 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<sub>2</sub> to C<sub>12</sub> and carboxylic acids C<sub>2</sub> to C<sub>12</sub> were identified in all film samples. 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 7, which presents the oxidation index as function of the air gap. In Figures 8 and 9 data obtained from MS analysis of volatile compounds present in the films after quenching are presented, as a function of the exposure time to oxygen at 325°C extrusion temperature. The MS results indicate that at shorter exposure times and/or lower processing temperatures aldehydes dominate over carboxylic acids. Similar to the oxidation index (Figure 7), the total amount of volatile compounds (TIC) seems to be dependent on the oxygen contact time, except for the very short air gaps where larger amounts were found. The latter results can be interpreted as a delayed release of degradation products formed in the extruder. The time needed for the release of these products as "extruder smoke" from the molten film surface might be longer than the time corresponding to 10 mm air gap, i.e., approximately 0.24 s. At longer exposure times the amount of degradation products increases drastically again. The aldehydes closely follow the TIC pattern, while the carboxylic acids behave differently with the oxygen exposure time. The acid compounds increased in the whole temperature interval investigated. The carboxylic acids may be formed through further oxidation of the aldehydes, or by direct oxidative degradation of the polyethylene. At lower extrusion temperatures and shorter oxygen contact times long-chain acids dominate, and there is a shift towards shorter carbon chain lengths, C<sub>2</sub> and C<sub>4</sub>, on increasing the extrusion process temperature and/or oxygen exposure times (Figs. 8 and 9).

At high temperatures and long exposure times dialdehydes were also identified, i.e., butadiol, pentaol, and hexadiol, in low amounts. It is assumed that



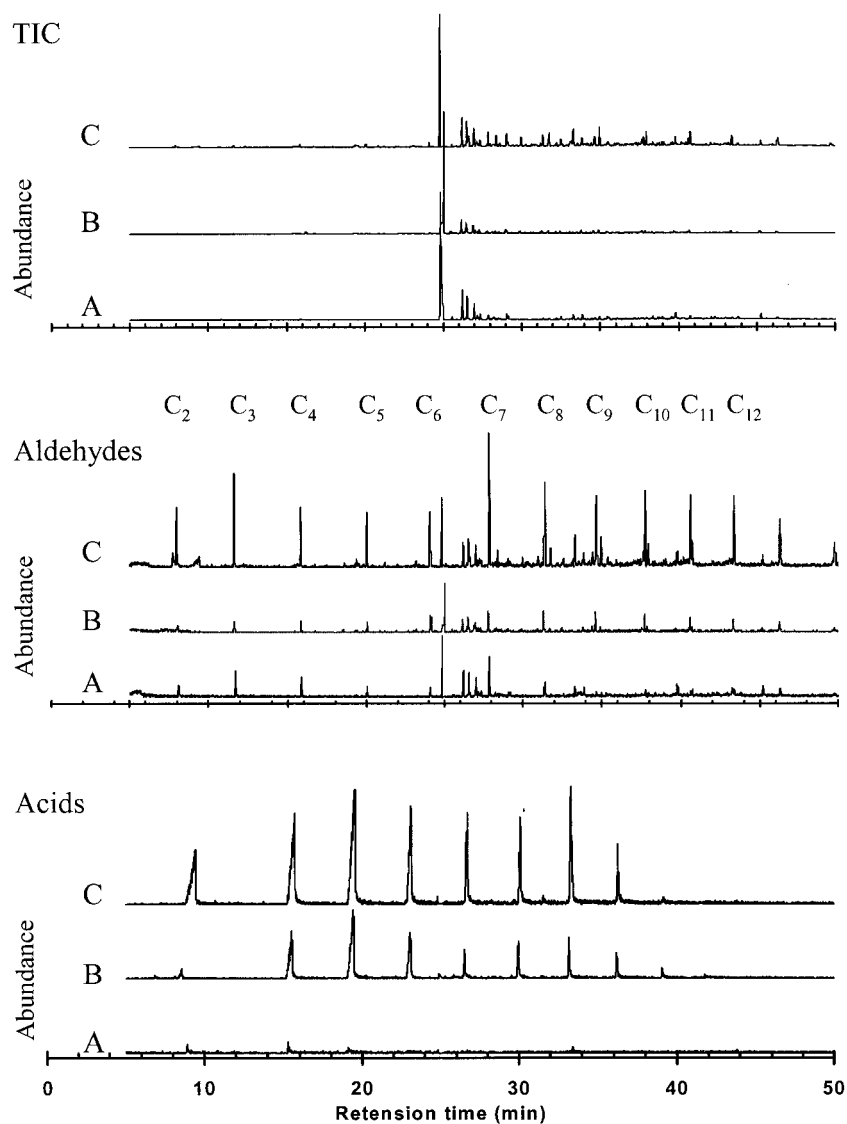
**Figure 8** GC-MS chromatograms obtained from LDPE films extruded at 325°C with different melt exposure times (A) air gap 10 mm, (B) 20 mm, (C) 40 mm, and (D) 80 mm. Chromatogram marked as TIC=Total Ion Count, as Aldehydes = ion count  $m/z=44$ , and as Acids=ion count  $m/z=60$ .

the dialdehydes are formed by a second radical attack on higher aldehydes, probably branched or unsaturated ones containing loosely bound hydrogens, leading to formation of aldehyde groups at both ends of the molecule.

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  $C_5 > C_4 > C_6 > C_7 \gg C_2$ , for LLDPE as  $C_5 > C_6 > C_4 > C_7 \gg C_2$ , for HDPE as  $C_5 > C_6 > C_7 > C_4 \gg C_2$ , respectively. In previous work<sup>9</sup> 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 oxidized 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.

Comparing the ion spectra from LDPE, LLDPE, and HDPE, in Figure 10, an interesting observation regarding hydrocarbon molecules may be done. For HDPE, which is the most linear polyethylene, significant peaks corresponding to decane, dodecane, tetradecane, hexadecane, and octadecane were found. For LLDPE smaller amounts of decane, tetradecane, and hexadecane were found while for LDPE only traces of hydrocarbons, presumably initiator carrier residuals, were observed. The hydrocarbons were present in all HDPE and LLDPE samples independent of extrusion temperature and are most likely oligomers formed in



**Figure 9** GS-MS chromatograms obtained from LDPE film extruded with 80 mm air gap processed at different extrusion process temperatures. (A) 260°C, (b) 300°C, and (C) 325°C. Chromatogram marked as TIC=Total Ion Count, as Aldehydes=ion count  $m/z=44$ , and as Acids=ion count  $m/z=60$ .

the polymerization process. There are probably also longer alkanes present in the films but they will not be observed due to the used analytical setup.

### CONCLUSIONS

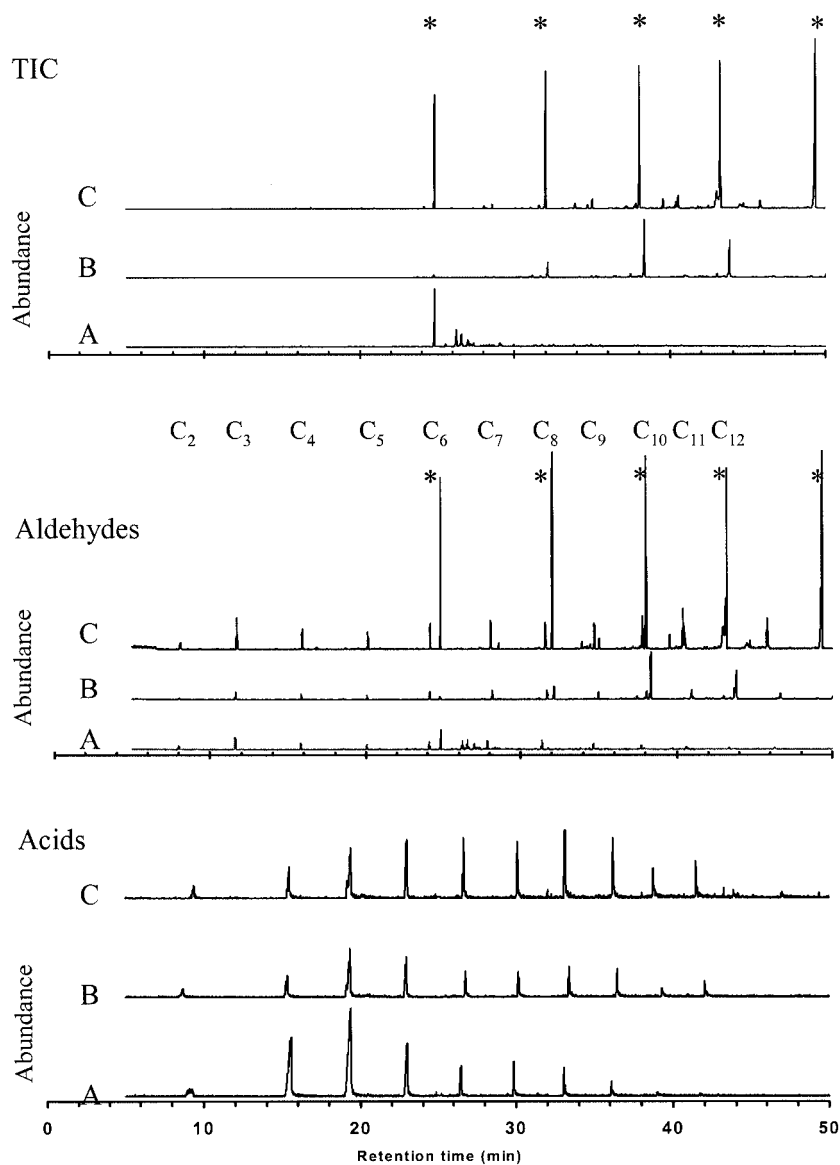
It could be concluded from this work that the degradation of polyethylene taking place in the extruder barrel, in addition to thermomechanical degradation, is dependent on the amount of oxygen present in the melt, and might be controlled by antioxidants, which interact with the formed radicals, and slows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

idant being present. The film degradation is a surface-related process.

The oxidized 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 oxidized  $C_2$ – $C_4$  compounds were found, while in the present work oxidized compounds ranging from  $C_2$  to  $C_{12}$  have been identified, 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



**Figure 10** GC-MS chromatograms obtained from (A) LDPE, (B) LLDPE, and (C) HDPE films processed at extrusion process temperatures of 315°C and 40 mm air gap. Oligomer esiduals identified as decane, dodecane, tetradecane, hexadecane, and octadecane, respectively, are marked with an asterisk. Chromatogram marked as TIC=Total Ion Count, as Aldehydes=ion count  $m/z=44$ , and as Acids=ion count  $m/z=60$ .

or acids were formed in the this location. Since these compounds may cause off flavor, it can be concluded that antioxidant additives should not be effective in preventing off taste or odor.

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