

Degradation of Low-Density Polyethylene During Extrusion. VI. Effects of Oxygen Content in Air Gap

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ABSTRACT: In our previous papers polyethylene degradation during extrusion coating has been studied and the type of degradation products that are formed and from which step they originate have been discussed. A trained sensory panel has rated the off-flavor intensities in water samples that have been in contact with various extruded films. Encouraged by the results from these investigations and the documented synergism between aldehydes and ketones and aldehydes and carboxylic acids in off-flavor intensity, the present study was aimed at confirming the belief that the off-flavor depends on the presence of oxidative degradation products that have migrated from the film into the water. By decreasing the oxygen concentration in the atmosphere surrounding the extruded melt presence of the highly oxidized species (i.e., carbonyl compounds and car-

boxylic acids) would decrease and thus the off-flavor in the water should decline. From this study it could be concluded that the extrusion temperature and the oxygen content in the atmosphere nearest the molten film before quenching are the most important parameters for oxidative degradation and residence time in the air gap influence the amount of oxidative degradation products formed. Furthermore we concluded that the off-flavor intensity is strongly correlated to the surface oxidation index of the film. Carboxylic acids are present in the water extracts of extruded films and are related to the off-flavor intensities. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1767–1775, 2005

Key words: degradation; polyethylene (PE); off-flavor; films; surface oxidation index

INTRODUCTION

Polyethylene (PE) is one of the most important polymers used in food packaging. Ethylene polymers degrade during processing and the contribution from the degraded PE to taste and odor has been investigated and reported in several papers.^{1–12} It is known that PE degrades by both thermal and thermal-oxidative mechanisms. In thermal degradation, unsaturated and some saturated hydrocarbon products are formed.¹³ For PE there is a critical melt temperature of 270–280°C, at which the oxidative degradation reactions start to increase dramatically, provided oxygen is available.^{9,10,12,13} Oxidative degradation of polyolefines follows an autooxidation reaction mechanism^{13–15} by hydroperoxide formation and decomposition, generating alcohols, aldehydes, ketones, and carboxylic acids.¹⁶ Polymer radicals formed in the

melt can react with oxygen, or combine to form larger molecules or crosslinked gels.⁹ Polymers containing additives such as antioxidants will also degrade, but the participation of the additive creates a more complex mixture of degradation products arising from degradation of the additive.¹⁷ Many of the oxidized degradation products are volatile at the extrusion temperature and evaporate from the polymer surface.¹

In our previous papers^{1,9–12,18} polyethylene degradation during extrusion coating has been studied and the type of degradation products that are formed and from which step they originate have been discussed.^{1,9–12} A trained sensory panel has rated the off-flavor intensities in water samples that have been in contact with the various extruded films. Encouraged by the results from these investigations and the documented synergism between aldehydes and ketones and aldehydes and carboxylic acids¹⁸ in off-flavor intensity, the present study was aimed at confirming the belief that the off-flavor depends on the presence of oxidative degradation products that have migrated from the film into the water. By decreasing the oxygen concentration in the atmosphere surrounding the extruded melt presence of the highly oxidized species (i.e., carbonyl compounds and carboxylic acids) would decrease and thus the off-flavor in the water should decline.

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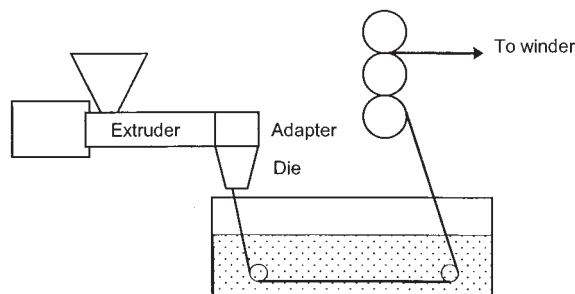


Figure 1 Film extrusion setup. The exposure distance for oxygen was adjusted by the water level in the water bath. The exposure distances were 20, 40, and 60 mm, equivalent to exposure times of 0.5, 1.0, and 1.4 s, respectively.

EXPERIMENTAL

Materials

The low-density polyethylene (LDPE) used in the study was CA 8200 (Borealis AS, Stathelle, Norway), with a melt flow index of 7.5 dg/min and a density of 920 kg/m³; granulates were used as shipped in PE bags, saturated with air.

Process equipment

Film extrusion was carried out with a laboratory extruder, Rheocord 90 (Haake GmbH, Karlsruhe, Germany), having a 19-mm screw diameter ($L : D = 24 : 1$; compression ratio = 4 : 1) and equipped with a Madoc shear module. The equipment used horizontal extrusion through a die turned 90° to a vertical position above a water bath (Fig. 1). Adjusting the distances between the die and the water surface regulated the melt exposure time to the air-gap atmosphere before quenching. Exposure times of 0.5, 1.0, and 1.4 s, equivalent to air gap distances of 20, 40, and 60 mm, respectively, were used. After the water bath a take-off unit wound up the film. With this setup the film samples were prepared. The take-off unit was set at a constant speed of 5.0 m/min and the extruder screw speed at 60 rpm, which gave a suitable film width and surface area. The extrusion process temperatures used gave polymer melt temperatures of approximately 280, 300, and 320°C (Table I).

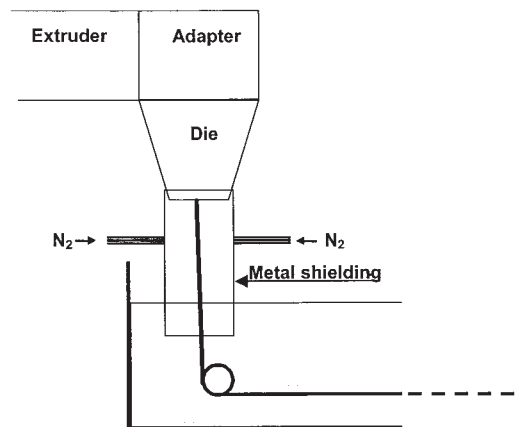


Figure 2 Film extrusion setup with control of the air-gap atmosphere. The exposure time (0.5, 1.0, and 1.4 s) for the gas was adjusted by the water level in the water bath.

To control the gas in the air gap a metal shield was formed from stainless steel (Fig. 2). The shield was equipped with two inlets for nitrogen gas, arranged to flow down along the metal surface without blowing directly at the molten film surface. This precaution was taken to prevent local cooling of the film and jeopardizing the consistency of film-surface temperature. The shield was used only in experiments where the air-gap atmosphere was to be kept free from oxygen.

Film sampling

The film extrusion was run for at least 45 min for equilibration at every new temperature profile before sampling, which was done in two ways. For the identification of degradation products the film samples were cut out at the winder stand without winding the film. The samples were placed into loosely wound coils wrapped in grease-free 18- μ m aluminum foil (Plus Pack AS, Odense, Denmark). Samples for off-flavor evaluation were taken as bundles of film sheets, without separation, by cutting the film coil and wrapping in aluminum foil. This procedure protected the sample from contamination and evaporation of low molecular weight material.

TABLE I
Extrusion Process Temperatures (EPT) Used^a

EPT (°C)	Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Zone 4 (°C)	Zone 5 (°C)	Zone 6 (°C)	Melt temperature (°C)
280	230	255	270	270	265	265	282
300	240	270	290	290	282	282	300
320	250	285	310	310	300	300	320

^a Zones 1–3, extruder barrel; zone 4, adapter; and zones 5–6, die.

Surface oxidation

Measurements of the total oxidation at the various film surfaces were taken by FTIR (Protégé 460 Spectrometer E.S.P., Nicolet Instrument Technologies, Madison, WI). 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). The ATR technique was used to examine the film surface layer. The spectra obtained were then evaluated by calculating the intensity ratio of the C=O stretching at 1720 cm^{-1} over the C—H vibration at 2660 cm^{-1} . This relation is reported as the surface oxidation index (SOI). The C=O stretching intensity was taken as the peak height at 1720 cm^{-1} ,¹⁹ using a horizontal baseline between 1670 and 1770 cm^{-1} . The intensity for the C—H vibration was taken as the peak height at 2660 cm^{-1} ,¹⁹ using a horizontal baseline between 2400 and 2450 cm^{-1} .

Off-flavor evaluation

Sample preparation

Water was used for sensory evaluation because of its neutral taste and the simpler detection of flavors.²⁰ Water used in the evaluation of off-flavor was activated carbon-filtered municipal tap water, which had been flushed for 4 h before collection in 2-L glass bottles. The water was referred to by the sensory group as having no taste of its own. Approximately 12.0 g of extruded film sample was put into a glass bottle before filling with 2000 mL water, which is approximately twice the amount of polymer film per liter as the food contact layer in a 1-L carton package. Two bottles were prepared per sample, and they were left undisturbed for 24 h at 23°C. From each of the two bottles 900 mL was taken and combined and used for the sensorial evaluation. The remaining 1100 mL from the bottles was combined and used for chemical analysis.

Evaluation procedure

A group of trained panelists consisted of 20 persons. In the sensory evaluation an unstructured, 120-mm linear scale (according to the ISO 6564-1985 9.1.3) was used. In one evaluation session four different samples were tested. The samples were served to each panelist in well-ventilated polystyrene cups (Duni Combi; Duni AB, Halmstad, Sweden) covered by poly(propylene) lids (watch glasses; Kartell, Noviglio, Italy). For each panelist the evaluation order of the samples were randomized. To facilitate further handling of data the 120-mm scale was rescaled to intensity scores 0–100 by dividing the ratings by 1.2.

Identification of oxidation products

Sample preparation of film

A small piece of film 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 balance (Mettler Toledo, Greifensee, Switzerland). The film sample was wound around a glass rod and put into a desorption glass tube [outer diameter (OD) 6.0 mm/inner diameter (ID) 3.9 mm; length 178 mm] from Gestel GmbH and Co. KG (Mülheim an der Ruhr, Germany). The tube was then placed in the sample rack of a thermo-desorption autosampler.

Analysis of film

The analytical setup consisted of a thermo-desorption unit (TDS-2), equipped with a thermo-desorption autosampler (TDS-A), from Gerstel. Through the desorption chamber a flow of 50 mL/min of He was passed. The desorption tube containing the film sample was equilibrated at 20°C and then inserted into the desorption chamber. The temperature was held at 20°C for 1 min 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), maintained at 275°C, to the cooled injection system (CIS-3, Gerstel) in the gas chromatograph. During desorption the He flow (50 mL/min) through 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 adjusted to a 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) equipped with mass selective detector (MSD 5971 Series; Agilent Technologies, Palo Alto, CA), was used. The column was HP-1 (crosslinked methyl siloxane) 60 m \times 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 maintained at 260°C for 4 min. The transfer line to the mass selective detector was kept at 280°C. The electron impact mode was used at 70 eV. The scanning was performed at m/z values between 30 and 350. The

resulting electron multiplication voltage was used in the standard spectra autotuning mode. Solvent delay was 5 min. The software used was Chemstation G1701AA (version A.03.00, Agilent Technologies).

Each film sample was evaluated in triplicates and between every two samples (six desorption runs), a blank, consisting of an empty desorption glass tube including the glass rod, was run to ensure the cleanliness of the column.

Analysis of water

Solid-phase extraction. Solid-phase extraction (SPE) is a preconcentration method where organic components in a liquid (water in our application) are adsorbed onto an adsorbent. The organic components are then extracted from the adsorbent by a small volume of organic solvent (dichloromethane). Because a large volume of water (1000 mL) and a small extraction volume (200 μ L) are used, the organic components are enriched up to 5000-fold. Each off-flavor-rated water sample was divided into two sample flasks.

Method. An internal standard was used, prepared by weighing 50 ± 1.0 mg of 1,2,4,5-tetrabromobenzene 97% (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), into a 10-mL volumetric flask and adding dichloromethane to the mark and mixing well. To a new 10-mL volumetric flask containing MeOH, 100 μ L of the tetrabromobenzene solution was added and the volume adjusted with methanol to 10 mL. The syringe was rinsed with the methanol solution, keeping the needle inside the methanol solution, and solution was mixed well.

The water sample was weighed (1000 ± 1 g) in a 1-L flask with screw cap (GL 45; Schott Glass, Duran). The pH was adjusted to 2 by adding 0.75 mL 37% HCl, P.A. quality (Merck, Darmstadt, Germany). The internal standard solution (200 μ L) was added to the sample. The bottle was capped and the sample was well mixed.

An end-capped solid-phase column (1 cm³), loaded with 100 mg Sorbent Isolute C18 (Sorbent Technology, Norwood, MA), was used.

The adsorbent was washed and activated before sample application. The washing was done by slowly sucking 2 mL dichloromethane through the adsorbent. The activation included slow suction of 2 mL methanol followed by 2 mL water (pH 2) through the adsorbent. The flow rate was regulated by the pressure in the vacuum chamber. The adsorbent was kept wet after the activation.

The adsorbent column was connected to the sample flasks. The sample was slowly sucked through the adsorbent in a Vac Elut SPS 24 vacuum chamber (Analytichem International, Harbor City, CA), driven by a water-jet pump at approximately 4 kPa underpressure.

When the whole sample volume had passed the adsorbent, sucking air through the column for 3 min dried the adsorbent. Water residuals on the inside of the adsorbent tube were removed with a small stick with cotton tip.

Each adsorbent was eluted slowly with 200 μ L dichloromethane (ultrasonically treated 5 min) by means of a syringe. When the adsorbent was totally wetted by dichloromethane, a 1-min extraction time was allowed before elution. The eluate was collected in a 300- μ L vial (Cronacol). The elution was stopped when all dichloromethane has passed the adsorbent. The vial was removed and immediately sealed.

The sample was analyzed by gas chromatograph HP5890 Series II (Hewlett-Packard, Palo Alto, CA), equipped with an MSD 5971 Series mass selective detector (Agilent Technologies). The GC-MS was equipped with a 60-m HP-1 (0.32 mm ID, 1.0 μ m phase thickness; Hewlett-Packard). The initial temperature was set at 35°C for 1 min then increased by 6°C/min to 225°, which was held for 27 min.

Identification of oxidized volatile components

Organic acids (acetic acid to hexadecanoic acid) were analyzed by integrating the ion-chromatograms at $m/z = 60$,²¹ except for propanoic acid. Propanoic acid was not included because it does not give rise to the $m/z = 60$ peak.

The aldehydes (butanal to dodecanal) were analyzed by integrating the ion-chromatograms at $m/z = 44$.²¹

The ketones were analyzed by integrating the ion-chromatograms at $m/z = 58$,²¹ and at $m/z = 85$.²¹

All peaks were integrated in the total ion count mode (TIC9 at the identified retention time) to obtain representative amounts of each component. The components were identified with G1701CA software (version C.00.00 21-Dec-1999, Agilent Technologies 1989–1999) and the NIST Mass Spectral Search Program with the NIST/EPA/NIH Mass Spectral Library (version 1.7a 07/18/2000) was also used.

RESULTS AND DISCUSSION

In this investigation degradation during film extrusion of one extrusion-coating grade of LDPE was studied. The polymer was extruded at different extrusion temperatures, air-gap exposure times, and at different oxygen concentrations in the atmosphere in contact with the molten film surface. From the perspective of degradation a low oxygen concentration close to the melt would be equivalent to a short exposure time and/or a lower extrusion temperature. If off-flavor depends on oxidated degradation products, this implies that the rated off-flavor intensity for water packed in such films should also be in a range

TABLE II
Experimental Setup and Surface Oxidation Index (SOI)
for Extruded Films

Sample	Extrusion temperature (°C)	Air gap (mm)	Exposure time (s)	Air gap gas	SOI
A	280	20	0.5	Air	0.04
B	280	60	1.4	Air	0.12
C	300	20	0.5	Air	0.19
D	300	40	1.0	Air	0.49
E	300	60	1.4	Air	0.64
G	320	20	0.5	Air	1.26
H	320	40	1.0	Air	2.95
I	320	60	1.4	Air	3.34
J	320	60	1.4	N ₂ + air	1.83
K	300	60	1.4	N ₂	0.05
L	280	60	1.4	N ₂	0.05
M	320	60	1.4	N ₂	0.04

with that experienced at lower extrusion temperatures. The films were extruded in a sequence where all films exposed to normal atmospheric conditions were extruded first starting with 280°C and ending at 320°C. Thereafter a metal shielding was put in place around the molten film (Fig. 2) and a flow of N₂ admitted. The films were then extruded in an atmosphere with decreasing concentrations of oxygen (Table II).

Surface oxidation

The surface oxidation was analyzed for all film samples, A–M, and the results are given in Table II. As the polymer melt exits from the extruder die it is exposed to oxygen in the atmosphere surrounding the polymer melt and oxidation occurs. This oxidation is a surface-related process.⁹ At the different extrusion temperatures (280, 300, and 320°C) oxidized degradation products are generated at different reaction rates as well as different reaction paths. If the atmosphere around the molten polymer is controlled at different concentrations of oxygen, the oxidative degradation would give different oxidation states of the products. In this study the atmosphere consisted of air (21% O₂) and pure N₂ (0% O₂), respectively. During extrusion at 320°C and 1.4 s exposure time (film I) it was observed that the film was completely wetted by water when exiting the water bath (Fig. 1). On extrusion of film J, after the N₂ sweep had been introduced, it was found that the film was partially wetted by water, although highly reduced relative to film I. It was assumed that the film had been exposed to an atmosphere containing a low oxygen concentration as a consequence of a too low nitrogen flow. After the nitrogen flow was increased, the film became non-

wetting (film M) and it was thus assumed the atmosphere around the polymer melt was oxygen free.

The results from the surface oxidation analyses given in Figure 3 show that the extrusion temperature and the oxygen content in the atmosphere near the molten film are important for the level of surface oxidation. The surface oxidation index for a film extruded in air with an exposure time of 1.4 s at 320°C (film I) was 3.4 units, whereas one extruded at 280°C (film B) was only 0.12. The results in Figure 3 are in line with the results from our previous studies regarding the influence of air-gap exposure time on surface oxidation.^{9,10} When the extrusion took place in nitrogen atmosphere at 320°C (film M), the oxidation index was shifted to 0.04. Films B (280°C, exposure time 1.4 s), G (320°C, air 0.5 s), I (320°C, air 1.4 s), and M (320°C, N₂ 1.4 s) (Table II) were selected for further evaluation.

Degradation oxidized products

Film

As shown with the GS-MS traces given in Figure 4 oxidized degradation products increased with extrusion temperature and exposure time to air. It is also evident from the figure that the oxygen content in the air-gap atmosphere is important for formation of oxidation degradation products.

As previously observed, increasing amounts of oxidized degradation products were formed when the temperature and residence time in the air gap increased. In films extruded at 320°C (G and I) the amount of aldehydes (ion 44) and carboxylic acids (ion 60, Fig. 4) increased significantly with air-gap exposure time. At 280°C (film B) only traces of al-

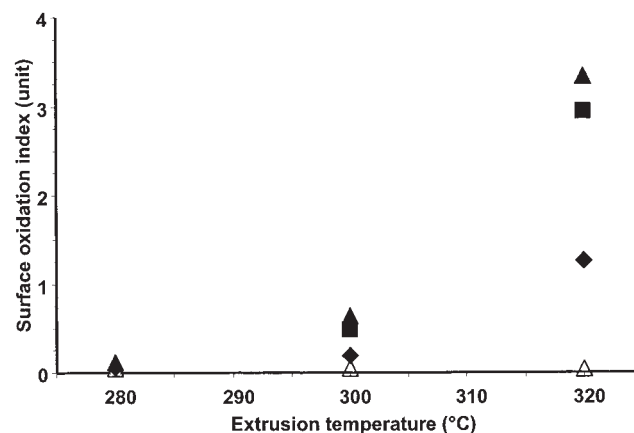


Figure 3 Surface oxidation index for LDPE extruded with air and nitrogen atmosphere at 280, 300, and 320°C and exposure time of 0.5 s (solid diamond), 1.0 s (solid square), and 1.4 s (solid triangle) in air and 1.4 s (open triangle) in nitrogen atmosphere.

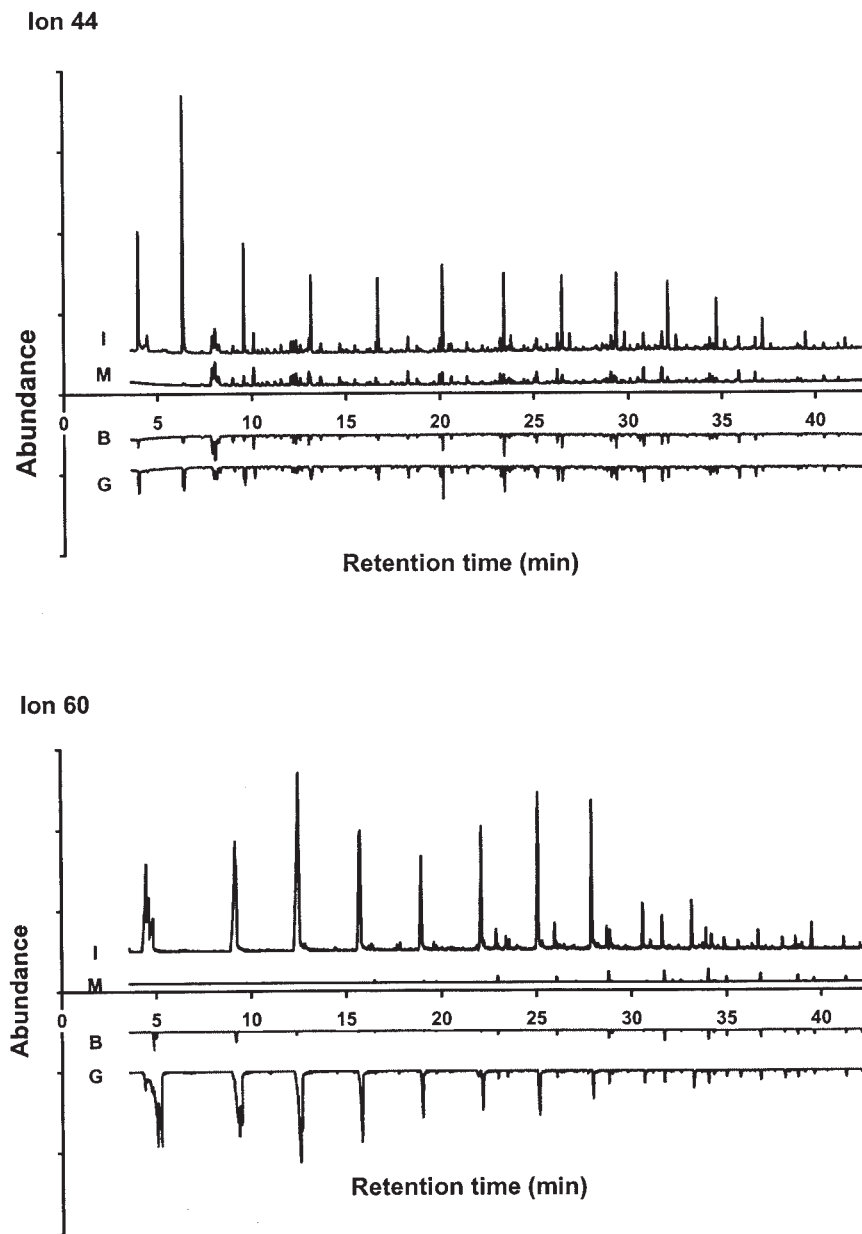


Figure 4 GC-MS analyses for aldehydes (Ion 44) and carboxylic acids (Ion 60) represented in film samples.

dehydes and carboxylic acids were observed. It can be noted that in nitrogen atmosphere no oxidation occurred in the air gap at 320°C (film M) and the level of aldehydes and carboxylic acids was very low. Independently of air-gap atmosphere no ketones were observed in any of the films, whereas great numbers of linear and branched alkanes and alkenes were found.

Water

In our previously reported studies^{10,11} a purge-and-trap method was used for identification of degradation products present in water, resulting in loss of information about the carboxylic acids in the water

phase. In this study a solid-phase extraction method (SPE), aimed to capture the carboxylic acids, was used.

The films analyzed above (B, G, I, and M) were stored in water for 23–24 h and the water extract was analyzed by SPE followed by GC-MS. The degradation products found in the water extract showed that oxidized compounds were the most abundant species. The highest concentrations were found in film I (i.e., the film having the longest exposure time to air at 320°C). Water extracts from films B (280°C, air 1.4 s) and G (320°C, air 0.5 s) showed considerably lower amounts of these degradation products. No oxidized products at all were found in the water extract from film M, which was extruded in nitrogen atmosphere at 320°C and 1.4 s exposure time. These results are in

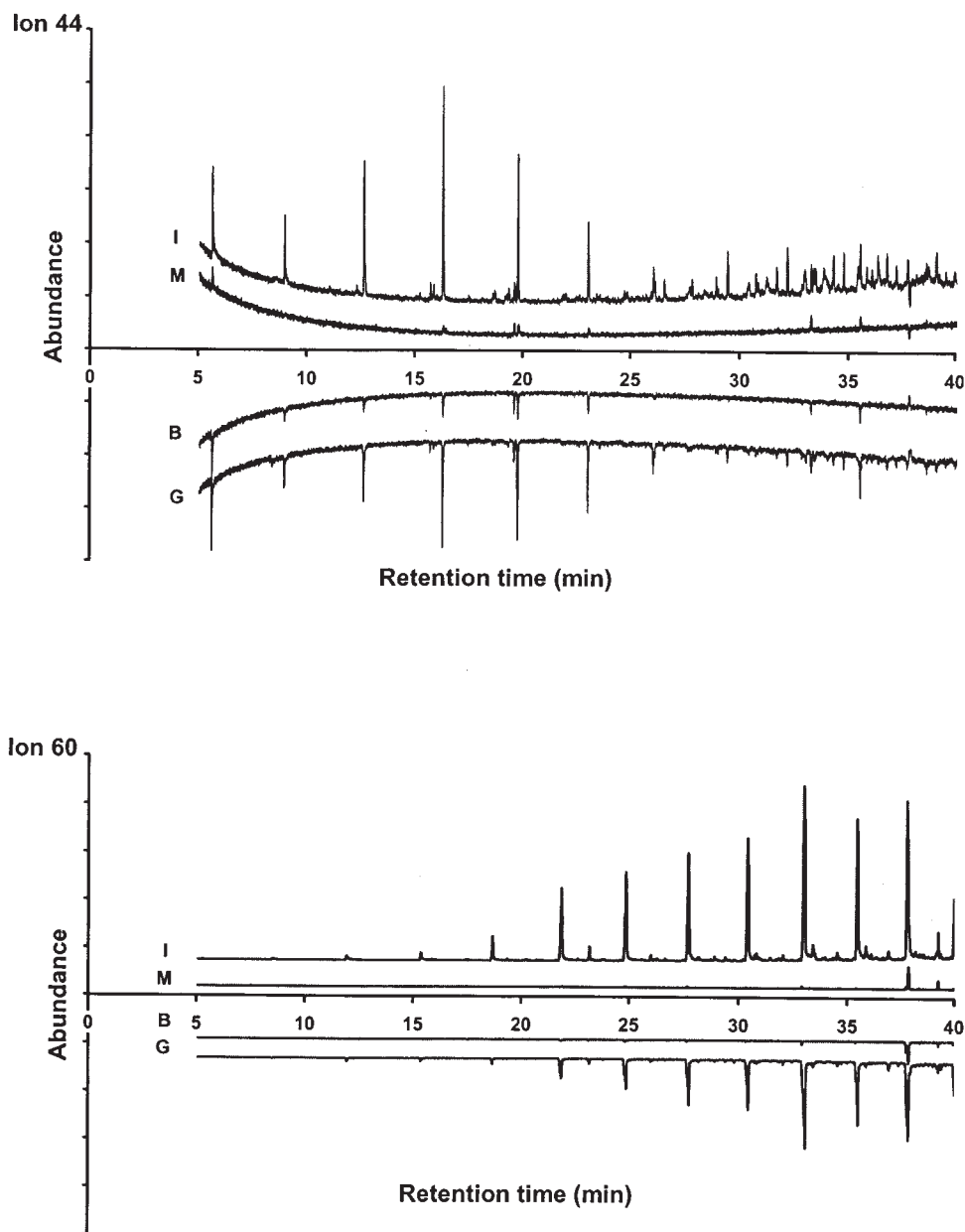


Figure 5 GC-MS analyses for aldehydes (Ion 44) and carboxylic acids (Ion 60) represented in water extracts.

accordance with the oxidation index results and the GC-MS results from film samples discussed above (Figs. 3 and 4).

Aldehydes identified in the samples, corresponding to the major peaks in GC-MS traces given in Figure 5, were pentanal to dodecanal.

Carboxylic acids (ion 60, Fig. 5), were found as a homologous series from butanoic acid to hexadecanoic acid, with a maximum abundance for dodecanoic acid. Some branched carboxylic acids were also found (such as 3-ethylheptanoic acid), at a retention time of 23 min. The presence of carboxylic acids in the water extracts found by the SPE method differed from the results obtained by the purge-and-trap method previously used and reported.¹⁰⁻¹² This is in line with

our thoughts that carboxylic acids are fully dissociated in the water and that their solubility is too high, which prevents them from volatilizing during the purge-and-trap analysis, as discussed in previous publications.

In water extracts of films exposed to air, large numbers of ketones (Fig. 6) were identified in the GC-MS traces (ion 58 and ion 85), including octanones, nonanones, decanones, and some diones, such as 2,15-hexadecanedione. Unsaturated degradation compounds were also indicated at retention times > 30 min.

In a previous study¹⁰ we reported that branched alkanes were predominant in the film before water extraction, whereas after extraction linear alkanes

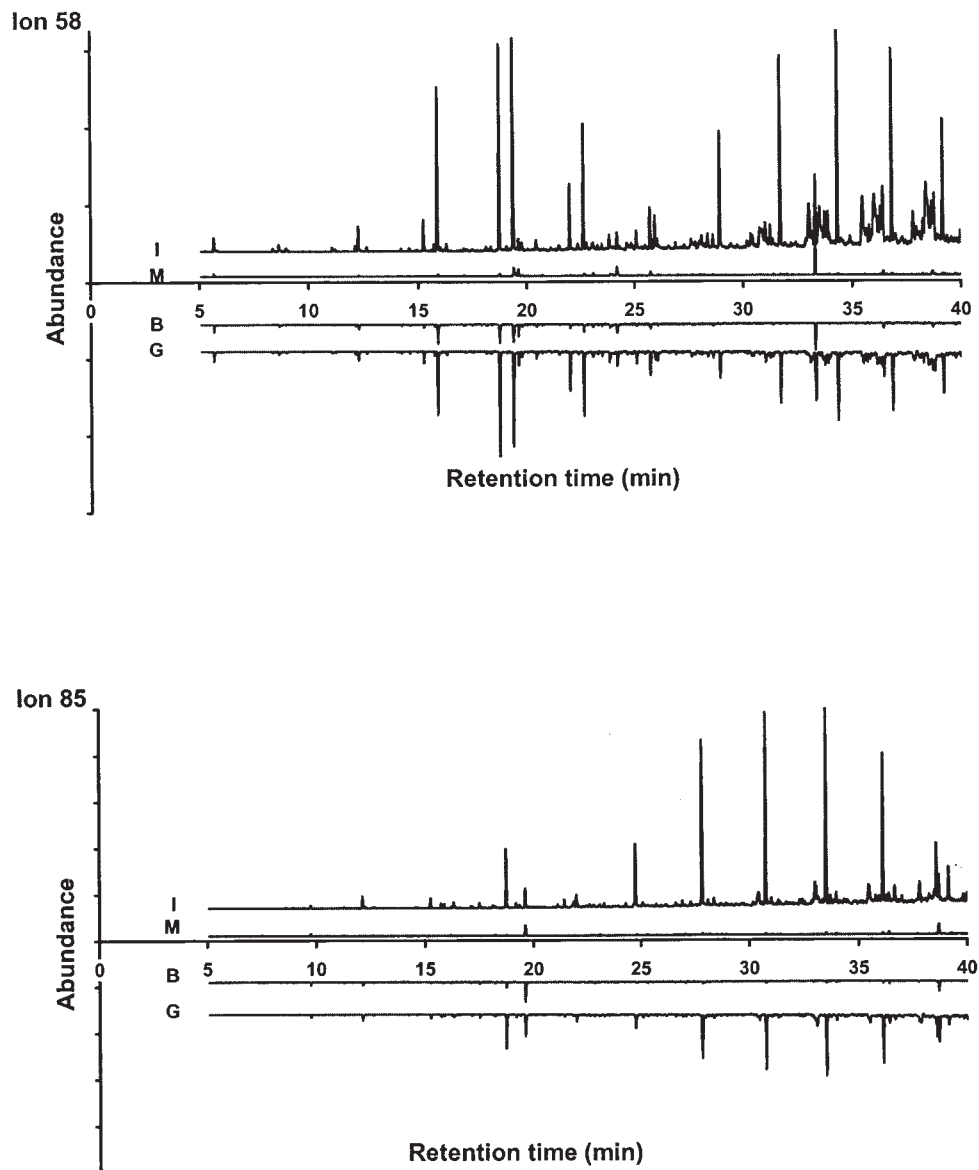


Figure 6 GC-MS analyses for ketones (Ion 58 and Ion 85) represented in water extracts.

were predominant. The observed ketones in the water extract in this study, as in the extract and film after extraction previous reported,¹⁰ might originate from reactions involving branched alkanes forming a ketone and a linear alkane at the film–water interphase.

The GC-MS trace for ion 85 (Fig. 6) showed a homologous series of substituted furanones, such as 5-pentyl-2,3-dihydro-furanone to 5-octyl-2,3-dihydro-furanone, at retention times of 24 to 39 min. This finding is in line with what has been reported by other authors for water exposed to polyethylene materials.²²

Off-flavor evaluation

Water extracts from films B, G, I, and M (Table II), which had been analyzed for oxidized degradation

products, were evaluated for off-flavor by a trained sensory panel. The off-flavor ratings were correlated to the SOI, as shown in Figure 7. In accordance with previously reported results, increasing extrusion temperatures in air gave higher ratings at the same air gap. The water extract from the film extruded in nitrogen atmosphere at 320°C gave a very low off-flavor rating, similar to that obtained for film B (280°C, 1.4 s) extruded in air.

Comparison between degradation products and off-flavor

When comparing the total amount of degradation products found by GC-MS reported as total ion count (TIC) with off-flavor intensities, it was found that the

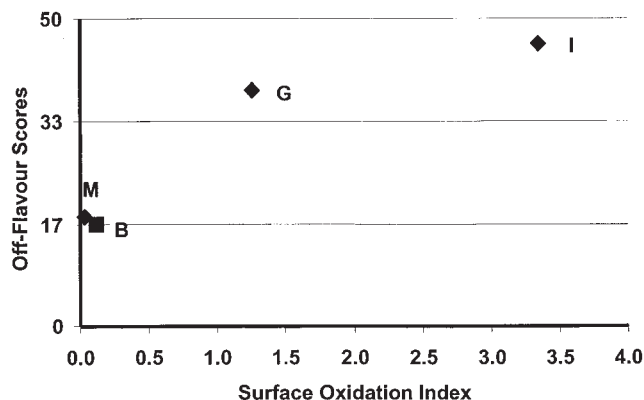


Figure 7 Off-flavor rating as a function of surface oxidation index for films extruded at 280 and 320°C with different air-gap atmospheres (see text for details).

TIC for all three films extruded at 320°C (G, I, and M) were approximately the same. The TIC includes oxidized degradation products as well as nonoxidized products such as saturated and unsaturated hydrocarbons. This leads us to believe that the total amounts of degradation products primarily consist of nonoxidized compounds and that the oxidized degradation products are the most important ones for recognizing off-flavor. Either these products are the off-flavor generators themselves¹⁸ or they are needed for carrying the off-flavor, imparting degradation products into the water phase by, for example, association.

CONCLUSIONS

From this study it could be concluded that:

- The extrusion temperature and the oxygen content in the atmosphere nearest the molten film before quenching are the most important parameters for oxidative degradation.
- Exposure atmosphere and residence time in the air gap influence the amount of oxidative degradation products formed.
- Degradation in the extruder itself has a minor influence on the formed oxidative degradation product in an extruded film.
- The off-flavor intensity is strongly correlated to the surface oxidation index of the film.

- Carboxylic acids are present in the water extracts of extruded films and are related to the off-flavor intensities.

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