

Degradation of Low Density Polyethylene During Extrusion. I. Volatile Compounds in Smoke from Extruded Films

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ABSTRACT: Many problems with odor and taste in food packaging can be traced to degradation of the packaging materials during processing. From this starting point, the degradation of polyethylene in a commercial extrusion coating process was studied by analyzing degradation products present in smoke sampled at the extruder die orifice. Two low-density polyethylenes, A and B, with similar melt flow indexes and densities and obtained from different producers, were investigated. A third polymer, C, consisting of recycled material B, was also investigated. More than 40 aliphatic aldehydes and ketones, together with 14 different carboxylic acids, were identified in the smoke. The highest concentration was found for acetaldehyde, regardless of polymer and processing conditions. Increasing the extrusion temperatures in the range 280–325 °C increased the amounts

of the oxidized products in the smoke. The extruded film thickness, 12 and 25 μm , influenced the concentrations of degradation products, with the thicker film giving higher amounts of product. The recycled polymer C generally gave lower concentrations of degradation products compared with the virgin polymer B. Differences in the product spectrum between the two virgin polymers may be related to differences in the manufacturing process. Many of the identified compounds have very characteristic taste and smell and are consequently of interest from an odor and taste point of view in food packaging applications. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1580–1586, 2002

Key words: polyethylene; extrusion; degradation; volatile compounds

INTRODUCTION

In the packaging industry, a large number of polymeric materials are used and converted into packaging materials by thermal processes such as film blowing, extrusion coating, and extrusion lamination. The materials are frequently used for packaging of different foods (e.g., liquids, chocolates, confectionery, and frozen foods). An important prerequisite for food packages is that they should not emit substances that interfere with the smell and taste of the packed products. Some compounds have a pleasant smell, whereas others have revolting odors and, in combination with food, undesirable flavors and tastes can be experienced.¹ The maximum migration of substances is regulated in various national legislations for food packaging materials and food contact layers.^{2–4} In polymer processing, as well as in the manufacturing of paper and board, degradation occurs.⁵ The degradation of the polymer molecule is related to thermal stress in combination with mechanical stress during processing

in, for example, an extruder. Under these conditions, the polymer chains degrade through chain scission reactions in combination with oxidation reactions. Oxidation can occur during extrusion in the extruder barrel through reaction with oxygen present in the polymer or at the die exit when the polymer melt comes into contact with surrounding air. The oxidized degradation products mainly consist of alcohols, aldehydes, ketones, and organic acids.^{6, 7} Many of these compounds have very characteristic taste and smell in very low concentrations (i.e., in the sub-ppb level).⁸ Different types of compounds generate different types of odor sensations.

It is known that polyethylene (PE) degrades by both thermal and thermal–oxidative mechanisms. In the thermal degradation, unsaturated and some saturated hydrocarbon products are formed.⁹ For PE there is a critical melt temperature of 270–280°C at which the oxidative degradation reactions start to increase dramatically.⁹ Oxidative degradation of a polyolefin follows an autooxidation reaction mechanism.^{9–11} via hydroperoxide formation and decomposition, with formation of alcohols, aldehydes, ketones, and acids.¹² Polymer radicals formed in the melt can react with oxygen or combine to form larger molecules or cross-linked gels. Polymers containing additives like anti-

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oxidants will also degrade, but the participation of the additive creates a more complex mixture of degradation products because of degradation of the additive.¹³ Many of the oxidized degradation products are volatile at the extrusion temperature and evaporate from the polymer surface. It should be mentioned that some of the organic acids (i.e., butanoic acid) have very strong influence on odor and taste.⁸

Degradation of PE has been studied under laboratory conditions at temperatures of 75 to 320°C without any applied mechanical stress. In the temperature range 75–200°C and in an environment containing 33–100% oxygen, 24 different degradation products were reported by Spore and Bethea.¹⁴ In this temperature range, the most dominant degradation products were aliphatic hydrocarbons. Thermooxidation of PE in an oxygen-containing atmosphere at temperatures of ~150°C was reported by Barabas and co-workers to give linear aldehydes and ketones, the most dominant compound being acetaldehyde.^{15, 16} Iring et al. claim that the hydroperoxide concentration is strongly dependent on the oxygen partial pressure and that the temperature (140–160°C) does not influence the peroxide concentration. For the whole temperature range, the reported degradation compounds were (except for water and carbon dioxide) hydrocarbons, alcohols, aldehydes, ketones, acids, cyclic ethers and esters, and hydrocarboxylic acids.^{7, 9–11, 13, 15–17}

The aim of the present investigation was to identify volatile compounds present in smoke from extrusion of low-density PE (LDPE) film in a commercial production extrusion coating line. The investigation was focused on oxidized products (i.e., aldehydes, ketones, and organic acids) that may cause off-flavor in foods. Most of the compounds identified in the smoke were present in low concentrations, close to the detection limit. Mainly a qualitative identification was made. It is assumed that compounds present in the smoke from the PE-melt would also be present in the polymer films from where they originate. In a food packaging material, they could consequently influence the taste of the packed food.

EXPERIMENTAL

Extrusion process

Extrusion of PE was carried out in a pilot extrusion-coating line. The extruder used, Er-We-Pa (Erkrath, Germany), had a screw of 3.5 in. in diameter and an length over diameter (L/D) ratio of 32. The extruder barrel was water cooled, and the melt temperature was measured and controlled between the extruder and the die. The average residence time for the polymers in the extruder was in the range 6–8 min. The extruder and die were held at different temperatures, relevant for the production of PE-coated board structures. The polymer mass temperature was set at 280 and

TABLE I
Process Data for Extrusion Process Set Up

Parameter	Film thickness	
	12 μm	25 μm
Line speed, m/min	250	250
Line speed, m/s	4.16	4.16
Air gap, m	0.30	0.25
Output, kg/(h · m)	180	375
Residence time in air gap, s ^a	0.144	0.120

^a Calculated as $t = (2 \cdot \text{air gap}/\text{line speed})$; assumed the velocity in the die is negligible compared with the line speed.

325°C. The temperature profiles used in the extruder were from the feeding zone to the die zone 240, 265, 285, 285, 285, 280°C, and 250, 290, 330, 330, 330, 320°C, respectively. The film thicknesses were set at 12 and 25 μm (Table I). The residence time in the air-gap was ~140 ms for the 12- μm film, and 120 ms for the 25- μm film.

Materials

Two commercial types of virgin PE [LD 256 (designated "A") and LDPE 707R (designated "B")], which were frequently used during the 1990s for extrusion coating, were used. The polymers were obtained from two different PE producers, Exxon Chemical and The Dow Chemical Company, respectively. A recycled polymer consisting of 100% recycled B, designated "C", was also used (see Table II). The polymers were of the autoclave reactor type and had melt flow indexes of 6–8, and a density close to 918 kg/m³. Different catalyst carrier systems were used by the manufactures of A and B. The recycled polymer C consisted of edge trims from extrusion coating of board with polymer B in a standard commercial process. The edge trims were regranulated at 190°C (Repak AB, Lomma, Sweden).

Sampling of extruder smoke

Sampling position was at the die orifice before the smoke entered into the exhaust hood. The smoke was sucked via a tube to the sample collection probes. The sampling of C₁–C₄ aldehydes and ketones was done by two different methods. In the first method, air was drawn through an adsorbent tube containing silica coated with 2,4-dinitrophenylhydrazine (SEP-PAK DNPH Silica, Waters Associates, Milford, MA,) reagent, as described by Colli et al.¹⁸ On elution of the SEP-Pak with 3 mL of acetonitrile, the hydrazine complex was eluted and prepared for analysis. In the second method, the exhaust air was drawn through an impinger flask containing 2 N HCl and 2,4-dinitrophenylhydrazine, as described by Kuwata et al.¹⁹ During sampling, reaction between aldehydes or ketones, respectively, and 2,4-dinitrophenylhydrazine formed a yellow complex. The sampling time was in the range

TABLE II
Sample Identification and General Properties for the Various Polymers

Property	Polymer A (LD 256)	Polymer B (LDPE 707R)	Polymer C (100% recycled B)
Supplier	Exxon Chemical	The Dow Chemical Company	
PE-type	LDPE	LDPE	LDPE
Melt index (dg/min)	8.0	7.5	6.2
Density (kg/m ³)	918	918	918
Branching	SCB 27.7/1000 C	NA	NA ^a
M _n	20 900	15 400	NA
M _w	174 900	113 000	NA
M _w /M _n	8.3	7.3	NA
Catalyst carrier type	Peroxide <C ₈ high purity low amount	Organic peroxide Odorless narrow cut Isoparaffinic solvent	Organic peroxide Odorless narrow cut Isoparaffinic solvent
Neck-in (mm) @ 325°C and 60 m/min (screw-speed)	73 (75 rpm)	45 (60 rpm)	30 (60 rpm)
Draw-down (m/min) @ 325°C (screw-speed)	400 (75 rpm)	300 (60 rpm)	150 (60 rpm)
Minimum film thickness (g/m ²) @ 325°C (screw speed)	8.2 (75 rpm)	2.0 (60 rpm)	6.2 (60 rpm)
Max tensile strength, MD/CD (MPa) (film thickness)	10.5/7.6 (15 μm)	13.2/12.4 (25 μm)	10.0/9.3 (25 μm)
Elongation at break MD/CD (MPa) (film thickness)	88.5/46.8 (15 μm)	457/457 (25 μm)	299/317 (25 μm)
Total volatile index per unit weight of polymer at 100°C	3 300	154 000	15 000

^a NA: not analyzed.

10–70 min. The airflow was regulated at 0.2 L/min for the SEP-PAK and 1.0 L/min for the impinger flask set-up. Sampling time was adjusted to collect equal volumes of the air/smoke mixture. Six different samples were collected per setting.

Two different techniques were used for the C₅–C₁₀ aldehydes, ketones, and organic acids. For sampling, the air was drawn through an adsorbent tube (Gilian Instrument Corporation, Wayne, NJ) containing either a single sorbent, Tenax 6×70 15/30 mg, or a combined sorbent consisting of 300 mg of Tenax TA, 60/80 mesh (Alltech Associates, Inc., Deerfield, IL) and 150 mg of activated charcoal 60/80 mesh (Carbosieve SIII, Supelco Company, Bellefonte, PA). The sampling time in these experiments was 100 min, with ~0.2 L/min airflow. The single adsorbent was transferred to a 3-mL vial, to which 2 mL of acetonitrile was added, and desorption took place overnight. The combined sorbent was thermally desorbed in a thermal desorption unit TDU MK V (Supelco Inc., Bellefonte, PA). The compounds desorbed were directly introduced into a gas chromatography (GC) capillary column. Six replicates were made per setting.

Identification of oxidation products

C₁–C₄ compounds

Liquid chromatography (LC) was used for detection of the aldehydes and ketones. The LC was equipped

with an ultraviolet (UV) detector (Varian Associates, Walnut Creek, CA) that recorded the concentration of the yellow hydrazone complex by measuring the UV absorption at 360 nm. A LC column of stainless steel (125 × 4 mm i.d.) was used. The column was packed with 5 μm LiChrosphere 100 RP-18e (Merck AG, Darmstadt, Germany). A pre-column (4 × 4 mm i.d.) packed with a similar stationary phase was used. The mobile phase was a mixture of A [60/30/10 (v/v) of water/acetonitrile/tetrahydrofuran] and B [40/60 (v/v) of water/acetonitrile]. The composition of the mobile phase was 100% A for 2 min and then a linear gradient reaching 100% B after 15 min. The flow rate was set at 1.5 mL/min. The detection limit for formaldehyde was ~10 μg/m³ air. For separation of acetaldehyde from propanal, a mobile phase consisting of 65/30/5 (v/v) of water/acetonitrile/tetrahydrofuran was used at the same flow rate as already mentioned. The water used was of Milli Q quality (Waters Associates, Milford, MA).

C₅–C₁₀ compounds

The analysis of C₅–C₁₀ aldehydes and ketones was performed by GC, and the various compounds were identified by mass spectrometry (MS). The GC-MS system (Hewlett-Packard, Palo Alto, CA) consisted of an HP 5890 II gas chromatograph equipped with an HP 7370 auto sampler and an HP 5971A quadrupole

TABLE III.
Aldehydes Found in the Smoke from Extruded Polyethylene^a

Property	Polymer				
	A	B	B	B	C
Temperature (°C)	325	280	325	325	325
Film thickness (μm)	25	25	12	25	25
Formaldehyde (mg/m ³ air)	4.1	0.2–0.3	1.6	4.3	1.9
Acetaldehyde (mg/m ³ air)	5.4	0.3–0.5	5.2	13.2	3.7
Propanal (mg/m ³ air)	2.4	D	D	3.2	2.9
Propenal (mg/m ³ air)	D	D	D	D	Nd
Butanal (mg/m ³ air)	D	Nd	2.8	6.9	2.0
C ₅ to C ₁₂	D	Nd	D	D	D

^a D indicates that the compound was detected but generally at the detection limit of 0.01–0.1 mg/m³; Nd indicates not detected.

mass spectrometer. The auto sampler was used in connection with a split/splitless injector system. The injector was held at 150°C, with the split valve kept closed for 1 min after injection. The column was held isothermal at 20°C for 1 min and then the temperature was raised at 15°C/min to 110°C, followed by an increase at 5°C/min to 260°C, where it was kept for 5 min.

The MS detector was used in the electron impact mode with the mass range set between *m/z* 29 and 250. The threshold value was set at 75 and the electron multiplier at 1800 V. The filament of the MS was turned on after 8.5 min. The temperature of the ion source was set at 173°C and the heated transfer line at 280°C. The capillary inlet pressure of the fused silica capillary column was 0.035 MPa. The column used was a DB-5 MS (30 m × 0.25 mm i.d.) with a film thickness of 0.25 μm (J&W Scientific, Folsom, CA).

Organic acids

An adsorption/thermal desorption technique was used for the analysis of organic acids. With a TDU MK V thermal desorption unit, substances adsorbed on activated charcoal were desorbed and introduced into a capillary GC column. The column used was a DB-5 MS (30 m × 0.25 mm i.d.) with a film thickness of 0.25 μm. To obtain a clean extract and facilitate the analysis of the organic acids, the absorbent tubes were first stripped of the more volatile compounds (e.g., hydrocarbons, aldehydes, and ketones) at 250°C. A second desorption was then performed at 265°C, and the organic acids were then transferred to the GC column and detected by MS.

RESULTS AND DISCUSSION

It is well-known that film extrusion of PE at high temperatures generates 'smoke'; that is, low molecular weight compounds that are released as an aerosol from the surface of the film when it leaves the die

orifice of the extruder. Some of these compounds can be related to the initiator carrier system used in the polymerization process, mostly hydrocarbons, but at the very high temperature of the polymer melt (i.e., 270–325°C, thermooxidative degradation of the polymer takes place at the extruder exit with formation of oxidized fragments of the degraded polymer.

Extrusion of three different PEs, A, B, and C, was carried out in a pilot extrusion coating line, at different temperatures and film thickness (Tables I and II). Polymers A and B came from different suppliers, using different initiator systems and initiators, and polymer C was a recyclate of polymer B. The exact compositions of the initiator systems were not disclosed by the manufacturers. Analysis of the smoke generated during extrusion of the polymers positively identified a large number of different oxidized degradation products, in varying concentrations (Tables III–V).

Aldehydes

Extrusion of the three polymers A, B, and C, at 280°C produced concentrations of C₁–C₃ aldehydes in the smoke just above the detection limit. At a melt temperature of 325°C, sizeable amounts of C₁–C₄ aldehydes were observed, as well as low but detectable concentrations of aliphatic C₅–C₁₀ aldehydes (generally at the detection limit of 0.1 mg/m³), as indicated in Table III. The measurable concentrations of aldehydes in the smoke increased by a factor of 10–20 with the temperature increase. This result clearly shows that both the rate of the oxidation reactions and the rate of evaporation of the degradation products increased rapidly in this temperature region. The dominant aldehyde was acetaldehyde (Table III), which also has been reported by Barabas et al.¹⁶ The homologous series of higher aldehydes found in small amounts in the present investigation has also been reported on thermooxidation of PE at 350°C by Mitera et al.⁶

TABLE IV
Ketones Identified in the Smoke at the Die Orifice for Extruded Films of Polyethylene^a

Polymer	Ketones
Polymer A	Propanone , 2-butanone , 2,4-pentadione, 2-pentanone , 3-methyl-3-pentene-2-one, 3-pentanone, 2-methyl-3-hexanone, 2-methylcyclohexanone, 3-hexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, 2-heptanone , 4-heptanone, 3-heptanone, 3-methyl-3 heptanone, 4-heptanone, 2-octanone, 3-octanone, 2-nonanone, 5-nonanone, 3-decanone, 3-undecanone, and 3-dodecanone
Polymer B	Propanone , 2-butanone , ethylcyclobutanone, 2-pentanone , 2-heptanone , and 3-dodecanone
Polymer C	Not investigated

^a Film thickness, 25 μm ; melt temperature, 325°C; all compounds were present in concentrations at the detection limit of 0.01–0.1 mg/m^3 ; the components in bold are those found in both polymer A and B.

The extruded film thickness influenced the formation and release of oxidation degradation products, as seen in Table III. At a film thickness of 12 μm and a temperature of 325°C the released amounts of C_2 , C_3 , and C_4 aldehydes detected in the smoke were more than a factor of two lower than those measured for a film thickness of 25 μm . The difference in the measured concentrations of volatile compounds in the smoke can be attributed to the difference in polymer volume being exposed to oxygen at the high temperature. Because of the constant line speed used, the surface exposed to oxygen per unit time at the different film thicknesses would be approximately the same. The residence time for the molten polymer in the air-gap would be a little longer for the thin film compared with the thicker one, depending on differences in line set-up (Table I). The thick film, with approximately the double mass of polymer present in the air-gap per unit time, would cool slower than the thin film, allowing degradation and oxidation as well as diffusion of degradation products to proceed for a longer time and at a higher rate. A larger amount of polymer would produce a larger amount of degradation products than a smaller one and, at similar ventilation fan speeds, this increased amount would result in a higher concentration of these products in the smoke. Another factor to be considered is that the polymer molecules would be exposed to high mechanical and thermomechanical stresses at the high screw speeds used for producing the thick film. A higher

number of reactive radical sites would be produced by the higher stresses, which on reaction with oxygen would give rise to a higher amount of oxidized fragments.

It was noted that some smoke components were more abundant than others depending on the polymerization process; for example, the type of catalyst and catalyst carrier system used by the manufacturer. This result can be observed when comparing polymers A and B. The concentration of acetaldehyde is at least twice as high and the butanal concentration is substantially higher in the smoke from polymer B compared with that from polymer A. It seems likely that the difference in catalyst carrier amount and type is responsible for this result. A similar effect was noted when comparing the concentration of degradation products obtained from polymers B and C, polymer C being a 100% recycled B polymer (Table II). As evident from the results in Table III, the aldehydes were generally present in significantly lower concentrations on extrusion of the recycled polymer as compared with the virgin one. This difference may be attributed to a lower concentration of solvent derived from the catalyst carrier, as indicated by the low total volatile index (Table II). The solvent should have evaporated during the first film extrusion. The total volatile index is related to the total integrated area of the gas chromatogram per unit weight of polymer and therefore is an indicator of the total amount of volatile carrier used. An alternative explanation might be that the most

TABLE V
Carboxylic Acids Identified in the Smoke at the Die Orifice for Extruded Films of Polyethylene^a

Polymer	Carboxylic acids
Polymer B	Acetic acid, propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, and dodecanoic acid

^a Film thickness, 25 μm ; melt temperature, 325°C; all compounds were present in concentrations at the detection limit of 0.01–0.1 mg/m^3 .

reactive sites present in the virgin polymer should have reacted at the first extrusion, whereas at the second extrusion, fewer reactive sites would be present and, as a consequence, lesser amounts of oxidized degradation products would be formed. It was observed that polymers B and C behaved quite differently on extrusion. During extrusion coating, the polymer film is stretched on exiting the film die (draw-down), and the thickness decreases several times in the air-gap because of viscous flow. The width of the extruded film decreases simultaneously due to the stretching (neck-in). High melt elasticity generally opposes the neck-in. The recycled polymer C had a significantly lower neck-in value, which was 2/3 that of the virgin polymer B (Table II). This result was a clear indication that the recycled polymer had high melt elasticity, presumably as a consequence of a broader molecular weight distribution with a high molecular weight tail due to radical recombination reactions during reprocessing. The stability of the melt curtain was less than that of the virgin B polymer and the draw-down value was lower. The low stability should partly be a result of the large number of gel particles present in the polymer C (reprocessed polymer B).

Ketones

In addition to aldehydes, a large number of ketones are formed on thermooxidative or UV radiation degradation of PE, as reported by Iring et al.,¹⁵ Hoff and Hacobsson,⁷ Barabas et al.,¹⁶ and Khabbaz et al.,¹⁶ among others. In the present study, ketones formed on extrusion of 25- μm films at 325°C from the virgin polymers A and B were determined by a combination of derivatization and liquid chromatography or GC-MS. A large number of ketones were positively identified, as indicated in Table IV. However, the concentrations of the ketones were low, generally at the detection limit.

Organic acids

It is a well-known fact that PE film surfaces contain highly oxidized species after exposure to high temperatures (i.e., 250–320°C^{7, 17}). The oxidized products contribute to the wetting and polarity properties of the PE film. In addition to aldehydes and ketones, small amounts of organic acids were detected in the smoke in the present study. The acids in the smoke were adsorbed on charcoal and then thermally desorbed and introduced into the GC-MS system. The peaks in the chromatogram representing the organic acids were rather broad but still significant.

Linear aliphatic acids from C₂ to C₁₂ were found in the polymer smoke, as reported in Table V, at an extrusion temperature of 325°C. All measurements were performed on extrusion of films with a film

thickness of 25 μm . Only small amounts of the acids were detected in the smoke. The concentration level of each acid identified was $\sim 0.1 \text{ mg/m}^3$. The polymer melt was exposed to atmospheric oxygen during a very short time (i.e., 0.1–0.2 s), which is presumably one reason for the low concentration levels of acids found in the smoke. The time for reaction with oxygen is governed by the distance between the extruder die orifice and the nip rollers, where the polymer melt is rapidly chilled and, consequently, further release of volatile components is prevented. At larger air-gaps, more acids should probably be formed and evaporated from the film surface. Also, very high polymer mass temperatures would increase the oxidation rate and compensate for short reaction time.

CONCLUSIONS

The amounts and distribution of degradation products generated on extrusion of LDPE in a commercial extruder line depend on the extrusion temperature and the extruded film thickness. High extrusion temperatures generate more compounds at higher concentrations in the smoke. Thick films cool more slowly and allow the oxidation to proceed at high rates before the film is quenched, thus releasing degradation compounds in higher amounts than from thin films.

The origin of the polymer influences the distribution of degradation products found in the volatile phase. Parameters such as catalysts and catalyst carrier systems, chain branching, and molecular weight distribution seem to influence the degradation pattern.

Recycled LDPE, compared with virgin LDPEs, releases less degradation products at lower smoke concentrations, presumably because reactive sites in the virgin polymer chains have reacted during the first extrusion and oligomers and catalyst carriers present in the virgin polymer should have evaporated.

The main oxidation products present in the smoke are aldehydes, with acetaldehyde being the most abundant product. Ketones and linear carboxylic acids are present in low concentrations. No alcohols were found, probably because the high extrusion temperatures (280 and 325°C) promoted heavy oxidation. More than 40 aliphatic aldehydes and ketones and 14 different aliphatic carboxylic acids were identified. Most of the identified oxidized compounds are potential sources of bad odor and taste in packaging materials applications.

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