

Degradation of Low Density Polyethylene During Extrusion. III. Volatile Compounds in Extruded Films Creating Off-Flavor

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ABSTRACT: This study was aimed at finding a correlation between the experienced off-flavor in packaged foods and the presence of specific degradation products in PE packaging films. The possibility to trap degradation products by chemical reactions with scavengers, that is, zeolites and maleic anhydride grafted LLDPE, were investigated. This trapping would prevent the degradation products from migrating to the polymer film surface and further into food in contact with the film. This work concludes that off-flavor in water packed in LDPE-films depends on extrusion temperature and the content of oxidation products in the polymer film. At lower extrusion temperatures, reactive additives to the LDPE material could control the release of off-flavor giving compo-

nents. Adsorbents, such as zeolites, which are able to adsorb degradation products, are effective also at higher extrusion temperatures. The amount of oxidized degradation products in the films correlated well to the perceived off-flavor in the packed water. The presence of aldehydes and ketones have a clear impact on the off-flavor. The best correlation between off-flavor and oxidized components were found for C₇–C₉ ketones, and aldehydes in the range of C₅ to C₈. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 847–858, 2005

Key words: polyethylene; degradation; degradation products; extrusion

INTRODUCTION

In all societies the demand for quality increases all the time. In this respect packaging in general, and more specifically food packaging, are increasingly in focus. The concept of quality is a very subjective one and depends on time, place, occasion, and the habits of the consumers. Considering the consumers' demands, the main quality parameters are appearance, color, texture, and flavor of the food. These parameters are classified as sensorial attributes and cannot directly be evaluated by physical–chemical analyses. More subjective methods have to be used, employing trained sensory panels and specific methodology. The perceived taste of a food itself depends on the taste of the food as well as on the package that the food was distributed in. Analytical instruments and procedures are continuously developed, and lower and lower con-

centrations of flavor components and contaminants can be detected. This fact leads to increased possibilities for evaluating and understanding the interaction between perceived off-flavor and chemical components present in the food.

Polyethylene, PE, is the most important polymer used in food packaging. Ethylene polymers degrade thermally^{1–3} during processing^{4–6}, and the contribution to taste and odor^{6,7} from the degraded PE has been investigated and reported in several papers. Because of the increased quality demands, there is an increasing interest to finding correlations between quality factors and marker substances for, for example, off-flavor. Storm van Leeuwen et al.⁷ have discussed the relation between the presence of aldehydes, ketones, and acids in extrusion coated polyethylene film samples and the off taste generated in food packed in the films. They also reported a synergistic behavior of aldehydes, ketones, and acids, giving off-flavor sensations even though the different components were below their threshold concentrations. Based on our previous work regarding degradation products found in extruder smoke⁴ and in extruded

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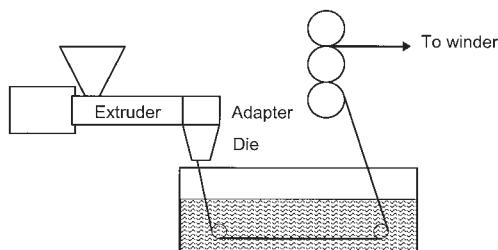


Figure 1 Film extrusion set-up. The exposure distance for oxygen was adjusted by the water level in the water bath. The exposure distance was 80 mm.

PE films,⁸ the present study was aimed at finding a correlation between the experienced off-flavor in packaged foods and the presence of specific degradation products in PE packaging films. In the present work, the possibilities to trap degradation products by chemical reactions with scavengers, thus preventing these components from migrating to the polymer film surface, and further into food in contact with the film, were investigated.

EXPERIMENTAL

Materials

LDPE

The low density polyethylene, LDPE, studied was CA 8200, Borealis, AS, Norway, with density 918 kg/m³, and melt flow index 7.5 g/10 min.⁹

Adsorbent

The inorganic adsorbent Abscent 3000 (89,768–2042000364, UOP, 25 East Algonquin Road, Des Plaines, IL, USA), was used in the investigation. This adsorbent has a hydrophilic structure that will have affinity for the degradation compounds.

Maleine anhydride copolymer

Maleine anhydride copolymer, MAH, Admer NF 358E, lot nr 77,655, from Mitsui Chemicals Cooperation, Japan, containing 0.1% grafted maleine anhydride and < 0.001% free maleic anhydride was used.

This grade is based on Linear Low Density Polyethylene, LLDPE, to which the maleic anhydride is randomly grafted. Admer NF 358E contains some antioxidants. The producer of the maleic grafted LLDPE has disclosed that they use phenolic and phosphite antioxidants as additives in their product.

Material preparation

Three different material samples were prepared. As a reference sample, pure LDPE was used as it was delivered in polyethylene bags. Blends of LDPE and 1 wt % Abscent 3000 and 10 wt % Admer NF 358E, respectively, were prepared. The materials were designated as LDPE, Zeolite, and MAH. For the preparation of the two blends, the desired amount of LDPE and the additive were weighed in a polyethylene bag and dry blended. The bag was agitated until a uniform mix was obtained and then supplied directly to the extruder and extruded without segregation.

Process equipment

For film extrusion a laboratory extruder, Rheocord 90, with a 19 mm screw diameter (L : D of 24 : 1, compression ratio of 4 : 1) and equipped with a Maddoc shear module was used. The equipment used horizontal extrusion through a die turned 90 degrees to a vertical position above a water bath (Fig. 1), which was used to control the exposure time to atmospheric oxygen. After the water bath, a take-off unit wound up the film. With this set-up the film samples were prepared. Adjusting the distances between the die and the water surface regulated the melt exposure time for atmospheric oxygen. An exposure distance of 80 mm was used. The take off unit was set at 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 exposure time for the molten film in contact with air was estimated at approximately 1.9 s. The used extrusion temperature profiles gave polymer melt temperatures of approximately 280°C and 315°C (Table I).

TABLE I
Extruder Temperature Settings in °C for the Two Temperature Profiles Used^a

Profile	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Melt temp
280	230	255	280	280	274	274	280
315	250	285	315	315	305	305	315

^a The extruder screw is zone 1–3, the adapter zone 4, and the die zone 5 and 6. The melt temperature is measured at the melt inlet in the die.

Film sampling

The extrusion process was run at least 45 min for equilibration at every new temperature profile before sampling was done. Sampling of film 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 loose wound coils wrapped in grease free 18 μm 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 Al-foil. This procedure protected the sample from contamination and evaporation of low molecular weight material.

Off-flavor evaluation

Sample preparation

Water was used for sensory evaluation due to its neutral taste and the easier detection of flavors.¹⁰ Water used in the evaluation of off-flavor was activated carbon filtered municipal tap water, which had been flushing for 4 h prior to collection in one-liter glass bottles. The water was judged by the sensory group, and referred to having no taste of its own. Approximately 3.50 g each of the extruded film samples were put into glass bottles prior to filling with 1000 mL water, This is approximately the same amount of polymer film as the food contact layer in a one-liter package. Three bottles were prepared per sample, and they were left for 24 h at room temperature (23°C) and thereafter served to the panelist in ventilated polypropylene cups. Random codes, which were different from one session to another, identified the samples. From each bottle 700 mL was used for the sensorial evaluation, and the remaining 300 mL from the bottles was combined and used for chemical analysis.

Evaluation procedure

A panel of 16 trained panelists carried out the sensory evaluations of the water after the film had been removed. The ratings of the off-flavor intensity on a scale from "No off-flavor" to "Very strong off-flavor" were done in accordance to the ISO 4120-1983 B3. The panel routinely tests packaging material off-flavor in water four times a week all the year round. Their normal ratings for polyethylene films are between "Weak off-flavor" to "Average off-flavor."

Three different evaluation sessions were performed at three different occasions. The first evaluation, Evaluation I, contained all 6 different film samples. This was done to evaluate the differences between the various samples. In this evaluation 13 panelists evaluated

the randomly presented samples. The second and the third evaluations, Evaluation II and Evaluation III, respectively, were done to evaluate differences between the samples extruded at 280°C and 315°C, respectively. In Evaluation II 13 panelists participated and in Evaluation III 12 panelists took part.

Identification of oxidation products

Sample preparation

Film. A small piece of the 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 (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 thermo desorption auto-sampler.⁸

Water. An internal standard was prepared by weighing 100.0 ± 1.0 mg of 1,4-dibromobenzene (CAS#106-37-6, 99%, Acros Organics, Geel, Belgium) into a vial, dissolved and diluted with dichloromethane (diChloromethane, Enviroscan 99.9%, Lab-scan, Stillorgan, Dublin, Ireland) to 10.0 mL. Of this solution 10 μL was added to 10.0 mL of methanol (Methanol pestiscan 99.9%, Lab-scan).

In a 100 mL stripper vial with side injection port, 100.0 g of water samples used in the sensory evaluation as described above were weighed in. Of the internal standard solution, 10.0 μL was introduced to the stripper vial under the liquid level. Before use, the vials were cleaned with 3% solution of a detergent (Extran MA02 neutral, Merck, Darmstadt, Germany) and rinsed at least five times with ultra pure water filtered through a Milli-RQ 6 PLUS with Millipore Purification Pak (Millipore SA, Molsheim, France) and stored in an oven at 150°C.

For identification of volatile organic compounds in the water phase, a dynamic headspace method was used. Helium gas (Scientific helium 6.0, Air liquide, Malmö, Sweden) was bubbled through the aqueous sample by means of a Dynamic Thermal Stripper (Model 1000, Dynatherm Analytical Instruments, Inc., Kelton, PA, USA). The volatile compounds passed together with the gas an adsorbent, Carbotrap 300 (200 mg Carbotrap B and 300 mg Carbotrap C) from Supelco (Supelco Park, Bellfonte, PA, USA). The adsorbents were preconditioned in reverse purge flow in a tube conditioner Model 60 Six (Tube Conditioner, Dynatherm Analytical Instruments, Inc. Oxford, PA, USA) at 265°C for 44 min with a 9 min cooling time prior to testing. The dynamic headspace analysis was run with a purge flow of 100 mL/min and a preheat

time of 15 min. To strip the volatiles from the water, a 25 min bubble time followed by an adsorbent drying time of 10 min was used. The temperature settings were 140°C, 70°C, and 65°C for the block, the oven, and the tube, respectively. After trapping the adsorbent tube was transferred to a thermal desorption system.

Analysis

Film. The analytical set-up consisted of a thermo desorption unit (TDS-2) equipped with a thermo desorption auto sampler (TDS-A) from Gerstel (Gerstel GmbH and 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, outer diameter (OD) 6.0 mm/inner diameter (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) 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 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 p.s.i., 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 auto-tuning mode. Solvent delay was 5 min. The software used was Chemstation G1701AA Version A.03.00 from Agilent Technologies.

Each film sample was evaluated in triplicate 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.

Water. Identification of oxidation products was performed with GC/MS. The set up consisted of a thermo desorption unit TDS-2 equipped with a thermo desorption auto sampler TDS-A from Gerstel. After equilibrium of the desorption chamber with He at a flow rate of 50 mL/min and 30°C, the sample tube (Gerstel, OD 6.0 mm/ID 3.9 mm, length 178 mm) was inserted. The temperature was held at 30°C for one minute for flushing the system from oxygen before increasing the temperature to 265°C with 60°C/min. The following analytical procedure was identical to the procedure for the film as described above.

Identification of oxidized volatile components. Organic acids (acetic acid to dodecanoic acid) were analyzed by integrating the ion-chromatograms at $m/z = 60$,¹¹ except for propanoic acid. Propanoic acid was not included because it does not give rise to the $m/z = 60$ peak as all other organic acids do.

The aldehydes (butanal to dodecanal) were analyzed by integrating the ion-chromatograms at $m/z = 44$.¹¹

The ketones, preferably methyl-ones, were analyzed by integrating the ion-chromatograms at $m/z = 58$,¹¹ and by the $m/z = 85$.¹¹

All peaks were integrated in the Total Ion Count mode, TIC, at the identified retention time to obtain representative amounts of each component. The most relevant peaks were also checked and identified by the retention times for the pure substances, respectively.

Correlations between off-flavor and oxidation compounds

Method

Two different methods have been used for finding correlations between the perceived off-flavor and the identified oxidation products. The total chromatogram areas and the number of peaks in each chromatogram were plotted versus the perceived off-flavor values. Regression analysis was used to correlate the values. Linear, exponential, and logarithmic regressions were evaluated for finding the best fit.

To identify which components are most likely to cause off-flavor in the water samples, the Simca P-8 software (Umetrics AB, Umeå, Sweden) for Principal Component Analysis¹² was used. To simplify statistical evaluation, the TIC chromatograms were recalculated with a time resolution of 0.04 min. The data sets were analyzed with the Partial Least Squares Projection to Latent Structures, PLS, model by the Simca P-8 software with the TIC per retention time as the predictor according to their contributions to off-flavor

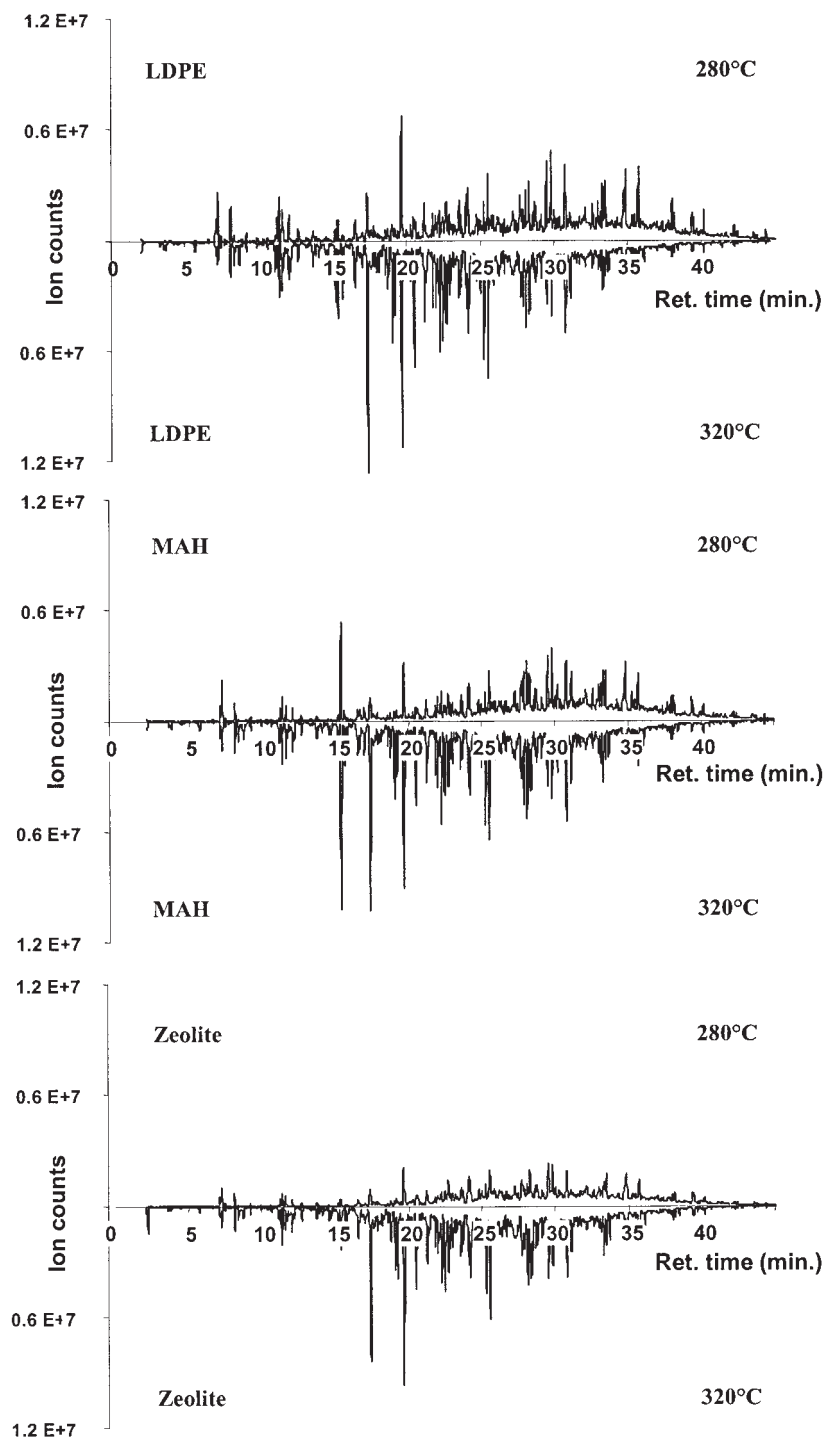


Figure 2 GC/MS chromatograms Total Ion Count for LDPE, MAH, and Zeolite films extruded at 280°C and 320°C.

intensity as the dependent.^{13,14} Through this technique compounds contributing most to the off-flavor variation could be identified.

To evaluate which of the volatile compounds correlated most to the off-flavor ranking, the Simca-P8 software program for Principal Component Discriminate Analysis,¹² PLSDA, was used.

RESULTS AND DISCUSSIONS

In our previous work^{4,8,15} it was discussed how the degradation of polyethylene is initiated at temperatures of 260–325°C. We identified the type of volatile degradation products being formed and where in the process most of the oxidative degradation

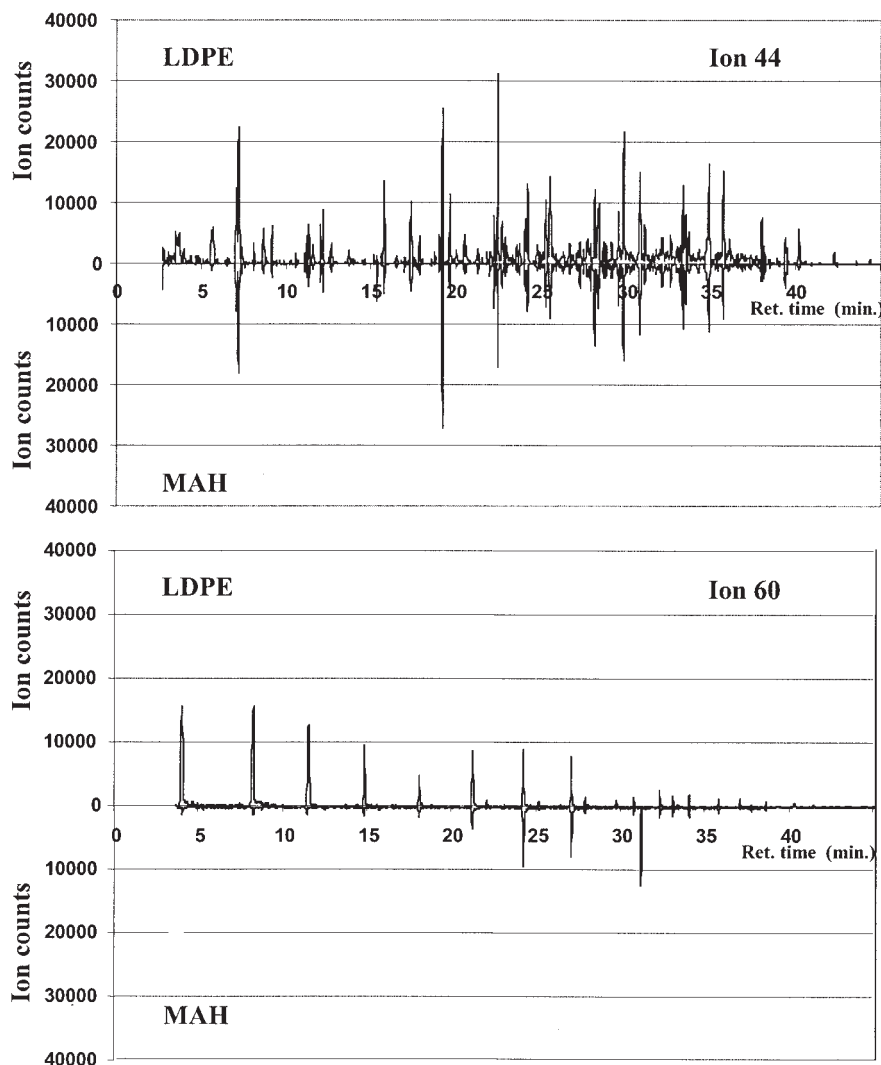


Figure 3 GC/MS chromatograms for LDPE and MAH films extruded at 280°C for the specific Ion Counts 44 (aldehydes) and 60 (carboxylic acids).

occurs. Studies by other authors^{16–18} have shown similar degradation product patterns even though degradation was conducted at lower temperatures. Alcohols and esters seemed to be more abundant at the lower temperatures and also dependent of ageing times.^{16–18} Against this background it is of interest to understand the relation between volatile degradation products and the off-flavor sensations they may induce.

The polymer investigated in this work was one LDPE grade aimed for extrusion coating. Virgin LDPE was compared to the same LDPE containing a zeolite adsorbent, and maleic anhydride grafted LLDPE, respectively. Virgin LDPE was used as a control for evaluating the changes resulting from different additives. The degradation products were believed to adsorb at the pore surface of the zeolite, preventing them from migration into the product.

The inorganic zeolites, which have an open porous structure, are active as adsorbents. The adsorbent also might have possibilities to capture the initially formed radicals and by that slow down the formation of oxidized volatile products. The aim of adding maleic anhydride grafted LLDPE to the LDPE material was to chemically capture the degradation products formed, especially alcohol intermediates, preventing them from further oxidation. The alcohols are likely to form ester compounds with the anhydride, which would bind them to the polymer and by that immobilize them. The hypothesis was that both methods should decrease the amounts of degradation products and prevent the polymer film from inducing off-flavor to water in contact with the film.

A sensory panel was used for evaluating of the off-flavor induced by the degraded polymer in packed water.

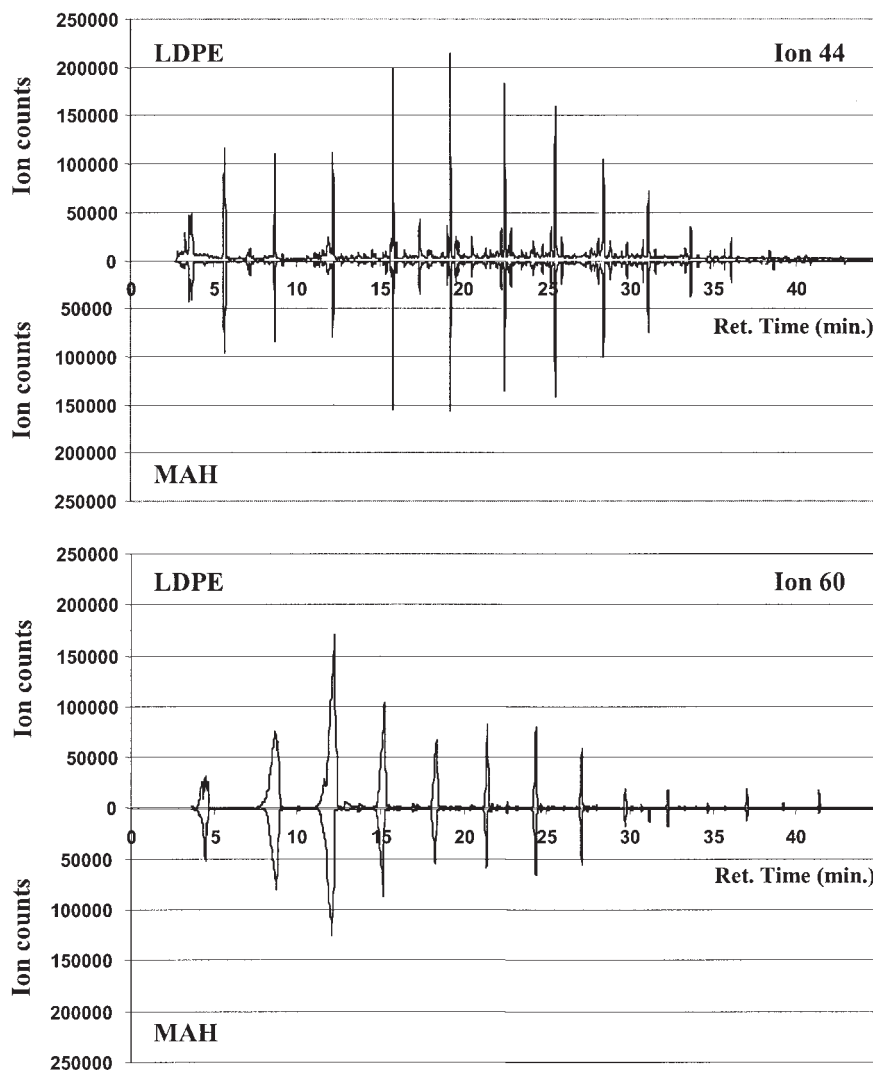


Figure 4 GC/MS chromatograms for LDPE and MAH films extruded at 315°C for the specific Ion Counts 44 (aldehydes) and 60 (carboxylic acids).

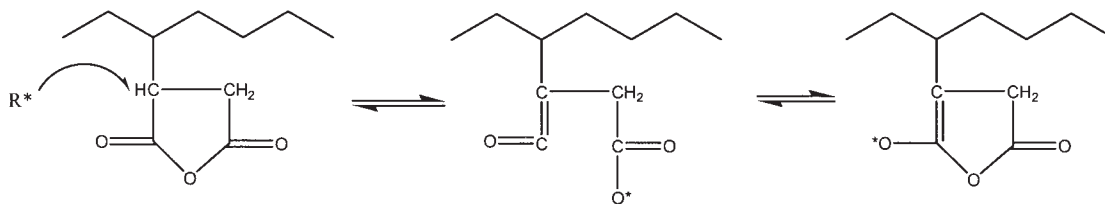
Oxidation products

The concentration of oxidative degradation products found during the extrusion of film, that is, aldehydes, ketones, and acids, increases for the LDPE material with the extrusion temperature increase and the residence time in the air gap as reported previously.^{8,15} All volatile compounds found were in the sub ppb to low ppb concentrations in all evaluated films. This was in accordance with our conclusions from previous works.

The zeolite-containing films showed similar degradation patterns as the reference LDPE film, except that the concentrations of volatile components in the films were much lower, as evident from the GC/MS data in Figure 2. This can be explained by the fact that the large active surface of the zeolite interacts and adsorbs the volatile degradation products. At higher temperatures the entropy term in the system increases, which favors desorption of the low molecular weight compounds.

The films containing maleic grafted LLDPE showed different results compared with the reference LDPE films at the lower extrusion temperature (280°C), the volatile products being present in significantly lower concentrations (Figs. 3 and 4). The aldehydes, identified as Ion 44 in Figure 3, were reduced to trace levels for most of the chain lengths, the remaining ones being present at similar concentrations as in virgin LDPE. Some of the oxidized degradation products, especially the C₂ to C₈ acids, identified as Ion 60 in Figure 3, had totally disappeared in the film prepared at 280°C, as compared to the LDPE reference film. At the higher temperature (315°C) this pattern was not observed (Fig. 4), and the concentrations of oxidized products were only slightly lower than in the reference.

There are two different possible explanations for the observed behavior. The maleic anhydride grafted polymer contains an antioxidant additive that could



Scheme 1

explain the lower levels of the degradation products found in the 280°C films. The producer of the maleic grafted LLDPE has disclosed that they use phenolic and phosphite antioxidants as additives in their product. The phenolic antioxidants react with oxygen-centered radicals, for example, free radicals from hydroperoxides, forming inactive products like alcohols and water. The phosphite antioxidant is able to react with hydroperoxides to yield inactive products, that is, alcohols. These alcohols might then react with the maleic anhydride grafted polymer forming esters, and by that being hindered to oxidize further, or to migrating into the water, causing off-flavor. This might not be the most likely explanation because the active concentrations of the antioxidants in the blend are very low, only one tenth of the concentration of the original additive in the maleic grafted LLDPE. In previous studies it had been concluded that antioxidants do not influence degradation of LDPE in the air gap.^{8,15} It can be suggested that the observed effect might depend on the possibility that the succinic anhydride groups in the maleic anhydride grafted LLDPE additive could act as radical scavengers by reacting with initially formed carbon radicals (Scheme 1).

The radical formed could be stabilized by the free electron pairs of the oxygen atoms. In the auto-oxidation sequence, initially formed degradation products like alcohols are likely to react with the anhydride groups to form ester compounds (Scheme 2).

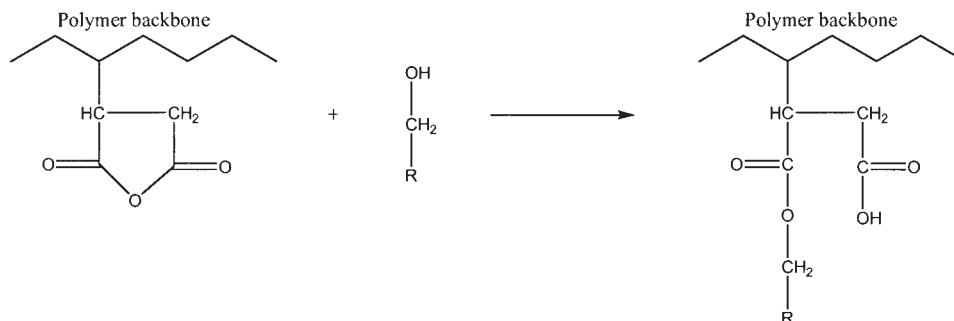
Compounds of this type have not, however, been found in the GC/MS chromatograms. This might be explained by the high molar mass of such an ester

compound, being nonvolatile and therefore not detected with the techniques used.

The oxidative degradation process occurs at the surface of the melt when it exits the die orifice, and continues until the melt is quenched.^{8,15} The number of radicals initiated by auto oxidation increases with temperature and the distance between the die orifice and the quenching point.^{8,15} At the higher extrusion temperature investigated, 315°C, few differences between the reference LDPE film and the MAH sample were observed (Figs. 3 and 4). As compared to 280°C, more acids were formed,¹⁰ as indicated by the differences found between Ion 60 ion chromatograms at 280°C versus 315°C. The successive oxidation from hydrocarbon via alcohol and aldehyde to carboxylic acid proceeds at higher rates at higher temperatures, and the stationary concentrations of the intermediate alcohols are therefore lower and the scavenging effect of the added maleic anhydride grafted LLDPE lower. There is also a possibility that the anhydride could be more stable than the corresponding ester at higher temperature. The stability of the maleic anhydride grafted LLDPE has also to be considered. The grafted polymer might degrade by oxidation or by reversal of grafting reaction, forming oxidized products and/or maleic anhydride. The unsaturated anhydride having a boiling point of 198°C¹⁹ would evaporate from the extruded film.

Off-flavor

The sensory evaluation results were clear and uniform in the ranking of off-flavor between the tested sam-



Scheme 2

TABLE II
Sensory Evaluation of Films Extruded at 280°C and 315°C for the Three Polymer Film Materials Studied^a

Material	LDPE		MAH		Absorbent	
	280°C	315°C	280°C	315°C	280°C	315°C
Melt temperature						
Evaluation I	0-1	4	0-1	4	0	2-3
Evaluation II	1	-	0-1	-	0	-
Evaluation III	-	3-4	-	3-4	-	2

Ratings: 0 = No off-flavor, 1 = Very weak off-flavor, 2 = Weak off-flavor, 3 = Average off-flavor, 4 = Strong off-flavor, 5 = Very strong off-flavor.

^a In Evaluation I all films were evaluated together. In Evaluation II and Evaluation III, the films having the same extrusion temperature were compared.

ples. Clear differences were noted between samples produced at the two tested melt temperatures. The off-flavor intensity increased for the high temperature extruded film due to higher concentrations of migrants. There were also clear differences in off-taste between the samples containing different additives. The results from the evaluations are listed in Table II. In Evaluation I all six samples were evaluated together. It was found that the zeolite at low extrusion temperature (280°C) was rated as "No off-flavor" and as "Weak to Average off-flavor" at the higher temperature (315°C). The MAH and the LDPE samples were both rated "No off-flavor to Very weak off-flavor" and "Strong off-flavor" for the low and high film temperatures, respectively (Table II). When testing samples having a relatively broad span in perceived off-taste, there is a risk that the scale can be compressed in the extremes. A selection of samples collected in accordance with the extrusion temperature used (Evaluation II and Evaluation III) gave more detailed information on off-taste differences, as seen in Table II. At the low extrusion temperature, Evaluation II, the zeolite sample was ranked as "No off-flavor," the MAH sample as "No to Very weak off-flavor," and the LDPE sample as "Very weak off-flavor." At the high extrusion temperature, Evaluation III, the ranking was "Weak off-flavor" for the zeolite, while the MAH and the LDPE films were rated as "Average off-flavor" to "Strong off-flavor."

Correlations between off-flavor and oxidized products

One of the main questions to be answered by the present investigation is: "Do the off-flavor test results correlate to the type of volatile components migrating from the films into the water and, if so, which components give the largest contribution to the off-flavor?"

To answer this question the total area count and the number of peaks in the different GC/MS ion chromatograms were plotted, respectively, versus the sensory panel responses. Linear, logarithmic, and exponential regression analyses were employed to evaluate if there were any correlations between the chromatographic data and the sensory responses. The best fit was obtained by linear regression. The regression coefficients, R^2 , for Total Ion Count (TIC), Ion 44 (aldehyde specific), Ion 58 (ketone specific), Ion 60 (acid specific), and Ion 85 (ketone specific) are given in Table III. In Figure 5 one plot illustrating good correlation (Ion 44) and one with no correlation at all (TIC) are given. It should be pointed out that different regression methods should not be used for the different ions.

As could be predicted, no correlation was obtained for the total peak area and number of peaks in the TIC chromatograms, respectively, and the sensory responses. Although the amounts of volatiles increase with extrusion temperature,^{4,8,15} they do not all contribute to off-flavor.

TABLE III
Linear Regression Coefficients (R^2) for Perceived Off-Flavor in Water Versus GC/MS Chromatogram Area and Number of Peaks in the Chromatogram, Respectively

GC/MS	Film before extraction		Water extract	
	R^2 TIC area	R^2 No. of peaks	R^2 TIC area	R^2 No. of peaks
Total ion count	0.0078	0.0000	0.3961	0.0000
Ion 44 (aldehydes)	0.9378	0.9290	0.7587	0.7123
Ion 58 (ketones)	0.9376	0.9062	0.0000	0.0000
Ion 60 (carboxylic acids)	0.9334	0.9390	0.0879	0.1856
Ion 85 (ketones)	0.5511	0.3446	0.9304	0.8588

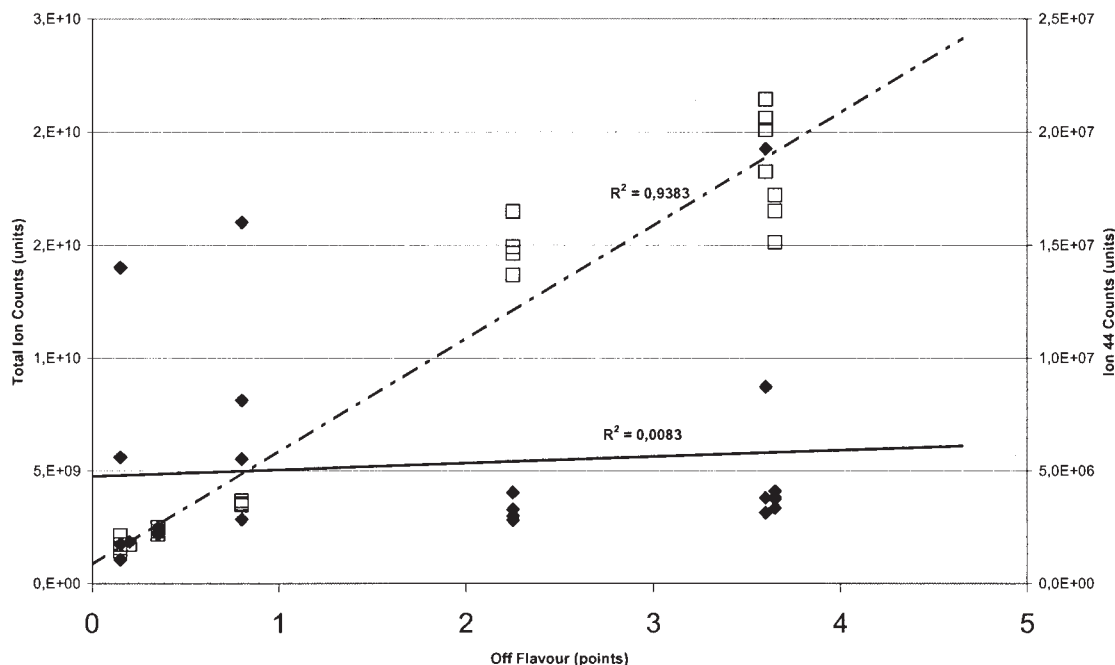


Figure 5 Off-flavor results as function of Total Ion Count GC/MS chromatogram area (filled diamonds) and Ion Count 44 GC/MS chromatogram area (open squares). Code for ratings, see Table II.

For the film samples good correlation was obtained for the areas of the ion chromatograms and the sensory panel ratings for Ion 44, Ion 58, and Ion 60, while the correlation for Ion 85 was not obvious. For the chromatograms obtained from the water samples, good correlation was found for Ion 85 and Ion 44, while the other ions did not correlate. It could be concluded that there was a strong relation between the presence of oxidized compounds in the films and the perceived off-flavor in water having been in contact with the film. Interestingly, there was no correlation for Ion 60, that is, carboxylic acids, for the water samples and the off-flavor ratings. This finding can be explained by the acids ($pK_a = 4.7-4.9$) being fully dissociated in aqueous solution at pH 7–8 at the low actual concentrations, and they may not vaporize from the aqueous solutions during the Purge and Trap analyses.

To find out which components are most likely to cause off-flavor in the packed water, Simca-P8 software¹² for Principal Component Analysis was applied to the LDPE film extruded at 315°C. The TIC chromatographic data as the predictors were tested against the perceived off-flavor data as the dependents. In Figure 6 the score plot from the PLS model analysis is shown. The data were generated from chromatograms of volatile compounds in the film before (1, 2, 3 in Fig. 6) and after extraction with water (7, 8, 9 in Fig. 6), as well as the chromatograms

from the purge and trap of the water itself (4, 5, 6 in Fig. 6). The score plot indicated that there were no significant differences in the triplicate of each sample, but there were significant differences between the film before exposure and after exposure to water and the water phase itself. In the loading plot (Fig. 7) all the chromatogram peaks were plotted and

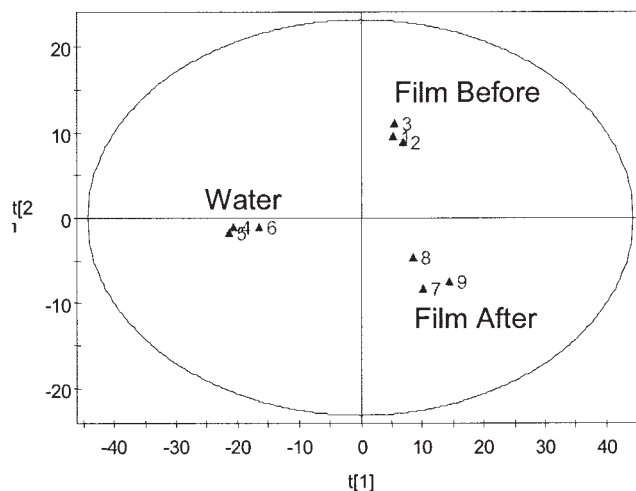


Figure 6 Score plots from SIMCA PLS analysis of GC/MS chromatograms for LDPE film samples extruded at 315°C, before (1,2,3) and after (7,8,9) water contact, and the water sample (4,5,6) have been compared.

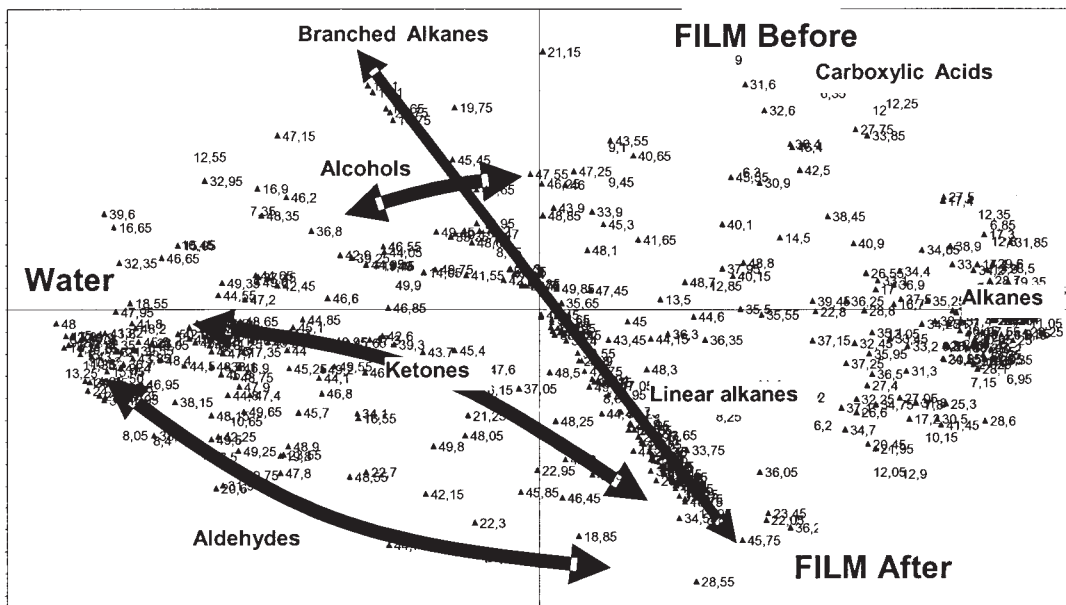


Figure 7 Loading plot from SIMCA PLS analysis of GC/MS chromatograms for LDPE film samples extruded at 315°C, before and after water contact, and the water sample. In the loading plot the position of the different volatile components are indicated by their retention times.

marked with their retention time, respectively. Superimposing the score plot (Fig. 6) over the loading plot (Fig. 7) revealed the most characteristic products present in the film before and after water contact, as well as those present in the water.^{13,14} From this it can be concluded that the most characteristic compounds present in the film before water exposure were the carboxylic acids. The acids were not present in the film after exposure to water. However, they should most likely be present in the water but were not detected because of the analytical technique used as discussed above. From Figure 7 it can be further concluded that the content of methyl- and ethyl-branched alkanes in the film changed during the water exposure. After exposure, they were neither found in the water nor in the film, while the amount of linear alkanes increased in the film. There was a domination of shorter aldehydes in the water and longer aldehydes in the film after exposure. Ketones from heptanone to decanone seemed to be characteristic for the water phase while not at all prominent in the film. All types of ketones were represented, from 2-heptanone, 3-heptanone, and 4-heptanone to 2-decanone and 5-decanone via linear octanones and nonanones. Alcohols were more abundant in the film after water contact than before, and alcohols were also found in the water phase (Fig. 7).

The PLSDA approach identified the most off-flavor giving compounds being ketones such as 5-nonanone, 2-nonanone, 3-heptanone, and 2-octanone, and aldehydes such as pentanal, hexanal, heptanal, and oc-

tanal. These findings were in line with the results found in the overall sensory evaluation of off-flavor in relation to the GC/MS chromatograms, as seen in Table III.

Other researchers have reported⁷ that the presence of carboxylic acids is needed to produce off-flavor by aldehydes and ketones present in the water at very low concentrations, probably by synergism. The effects on off-flavor from the carboxylic acids in the present system are an unsolved issue and will be further investigated.

CONCLUSIONS

From this work it could be concluded that off-flavor in water packaged in LDPE-films depends on extrusion temperature and the content of oxidation products in the polymer film. At lower extrusion temperatures reactive additives in the LDPE material could control the formation of off-flavor giving components. Adsorbents, such as zeolites, which are able to adsorb degradation products, are effective also at higher extrusion temperatures. The amount of oxidized degradation products in the films correlated well to the perceived off-flavor in the packaged water. The presence of aldehydes and ketones have a clear impact on the off-flavor. The best correlation between off-flavor and oxidized components were found for C₇-C₉ ketones, and aldehydes in the range of C₅ to C₈.

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