

# Susceptibility of Starch-Filled and Starch-Based LDPE to Oxygen in Water and Air

MINNA HAKKARAINEN, ANN-CHRISTINE ALBERTSSON, SIGBRITT KARLSSON

Department of Polymer Technology, The Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden

Received 11 September 1996; accepted 15 March 1997

**ABSTRACT:** The susceptibility of starch-filled and starch-based polyethylenes to oxygen in water and air was analyzed and compared. LDPE containing 7.7% starch and a pro-oxidant formulation in the form of masterbatch (LDPE-MB) was compared to pure LDPE, LDPE with 7.7% starch (LDPE-starch), and a blend with 70% starch and 30% ethylene maleic anhydride (starch-EMA). Thermal ageing at 80°C in air and water was followed by monitoring the molecular weight changes, the formation of carbonyl groups, and degradation products by SEC, FTIR, and GC-MS. It was demonstrated that LDPE-MB was the most susceptible material to degradation in both environments, although the degradation was faster in air than in water. The slower degradation in water is explained by a deactivation or leaching out of the pro-oxidant during the aging. The degradation of pure LDPE and starch-EMA is faster in water than in air. LDPE-starch was the only material that did not degrade during 11 weeks in water at 80°C. The addition of starch to LDPE made this material even more stable than pure LDPE to aging in water. The molecular weight distribution of LDPE-MB narrowed during aging in air. In water, on the other hand, the MWD of LDPE-MB, LDPE, and LDPE-starch broadened. The lower oxygen concentration in water increases the probability for molecular enlargement reactions in comparison to the case in air. Mono- and dicarboxylic acids were the major products identified in both environments. Ketoacids were formed in both air and water, but ketones and hydrocarbons were only identified after aging in air. Either these products are not formed or they remain in the polymer matrix rather than migrate out into the water. Lactic acid and 2-furancarboxaldehyde were only identified in the starch-EMA material degraded in water at 80°C. LDPE, LDPE-starch, and starch-EMA did not form any degradation products during 11 weeks at 80°C in air in agreement with the negligible molecular weight changes observed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 959–967, 1997

**Key words:** starch-filled LDPE; starch-based LDPE; oxygen in water and air

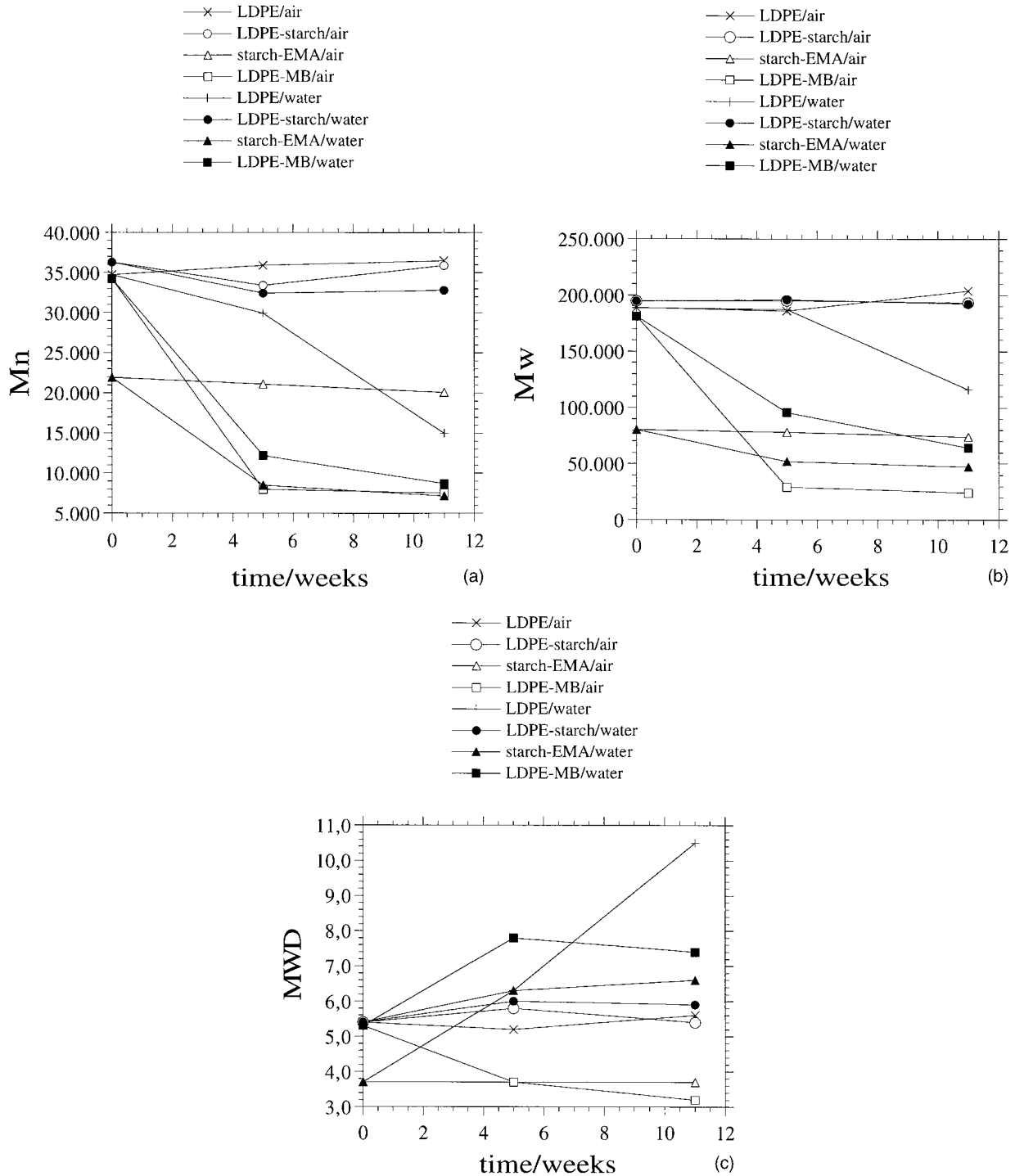
## INTRODUCTION

The environmental degradation of synthetic polymers is enhanced by biodegradable additives like corn starch.<sup>1,2</sup> When the biodegradation of the additives takes place, this weakens the polymer matrix and increases the surface to volume ratio, hydrophilicity, and permeability of the material and

the subsequent oxidative degradation of the polymer matrix is facilitated. Several studies have shown that the starch content of starch-filled polyethylene decreases during composting or burial in soil.<sup>3–6</sup> However, at low starch concentration in the absence of significant polymer degradation via thermal oxidation, part of the starch remains isolated within the polymer matrix and is unavailable for biological degradation.<sup>7</sup> Biodegradation rate is increased by prooxidant formulations, which give rapid thermal oxidation of the polymer matrix at temperatures as low as 40°C.<sup>8</sup> Prooxidants initiate degradation by producing

Correspondence to: S. Karlsson.

*Journal of Applied Polymer Science*, Vol. 66, 959–967 (1997)  
© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/050959-09



**Figure 1** (a) the number-average molecular weight, (b) weight-average molecular weight, and (c) molecular weight distribution of LDPE-MB, LDPE-starch, starch-EMA, and LDPE as a function of degradation time at 80°C in air and water.

free radicals that react with molecular oxygen and possibly also with the carboxyl and ketone groups in the oxidized polyethylene. The biodegradation of high molecular weight LDPE proceeds slowly,<sup>9</sup> but if the molecular weight is lowered by oxida-

tion, the microbial degradation of both polyethylene and the starch component isolated inside the polymer matrix is possible. Several studies show that the addition of a prooxidant is an essential requirement for thermal degradation of the poly-

mer matrix at low temperatures.<sup>3,7,10–12</sup> Loadings higher than 40 wt % starch must be employed, if starch alone should act as an enhancer of the degradation of PE-starch blends without the help of prooxidant additives.<sup>13</sup>

We have earlier proposed a mechanism for the biodegradation of polyethylene<sup>14</sup> and could recently show that microorganisms assimilate the carboxylic acids formed during the degradation of LDPE.<sup>15</sup> The thermal degradation of LDPE modified with starch and/or prooxidant according to Griffin technology gives rise to complex patterns of degradation products.<sup>16,17</sup> The aim of the present study was to compare the susceptibility of polyethylene modified with starch and/or prooxidants to oxygen in air and water by monitoring the molecular weight and functional group changes and by correlating these with the degradation products formed.

## EXPERIMENTAL

### Materials

Low-density polyethylene (LDPE) films (30  $\mu\text{m}$ ) were made by a conventional blown film process using a Betol extruder with a 25-mm screw of L : D 20 : 1, a blow-up ratio of about 2.5 : 1, and a die temperature of 185°C. The polymer was a conventional LDPE grade of MFI 2 acquired from ATO (France) with a conventional thermal stabilizer of undisclosed composition. The polyethylene films contained 7.7% starch (LDPE-starch) or 20% masterbatch (LDPE-MB) to promote degradation. The master batch consists of corn starch (7.7%), styrene-butadiene copolymer (SBS), manganese stearate, and linear low-density polyethylene (LLDPE). The behavior of the starch-modified materials was compared to polyethylene (LDPE) films without additives. In addition, the degradation of small granules of an injection-molded starch-based blend was studied (starch-EMA). This material contained 70 wt % corn starch and 30 wt % of ethylene maleic anhydride copolymer (EMA). The maleic acid content was approximately 0.8 mol %.

### The Degradation Procedure

The different materials were thermally aged at 80°C both in water and in air. The aging took place in an oven in closed glass vials, 100 mg of polymer in each vial. After 0, 5, and 11 weeks degradation products, molecular weight changes

and changes in the functional groups on the surface of the material were analyzed.

### The Extraction Procedure

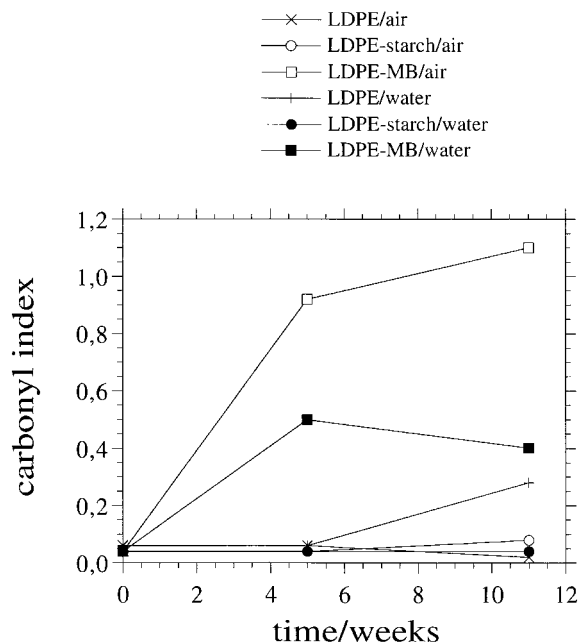
Diethyl ether (1 mL) was added to the air samples to extract the degradation products from the polyethylene films. After 1 h the diethyl ether was separated from the solid polymer and evaporated to dryness. The products were dissolved in 50  $\mu\text{L}$  hexane. The hexane fraction was removed and the hexane insoluble products were dissolved in 50  $\mu\text{L}$  0.1% HCl in methanol. Water samples were extracted with C18 solid phase extraction (SPE) columns. The columns were first activated with methanol (1 mL) and conditioned with pH 2 water (1 mL). After that, the pH of the water with the water-soluble degradation products was adjusted to pH 2 with HCl. One milliliter of the sample water was then allowed to penetrate the solid phase column. The column was slightly dried and the products were eluted with either 1 mL methanol or 1 mL 0.1% HCl in methanol. The methanol fractions were evaporated to 50  $\mu\text{L}$ . The 0.1% HCl in methanol fraction was warmed 15 min at 60°C to methylize dicarboxylic acids. The concentrated hexane and methanol fractions were then subjected to GC-MS analysis.

### Gas Chromatography-Mass Spectrometry (GC-MS)

A Perkin-Elmer 8500-model gas chromatograph with a split/splitless injector was connected to a Perkin-Elmer Ion Trap (ITD) mass spectrometer. The column used was a DB-WAX capillary column from J&W (30 m  $\times$  0.32 mm i.d.). The column temperature was held for 1 min at 50°C, then raised to 240°C at 8°C/min and finally held for 15 min at 240°C. Helium was used as a carrier gas. The samples were introduced in the splitless injection mode at 225°C. Some samples were also analyzed with a Finnigan SSQ 7000 mass spectrometer coupled to a Varian gas chromatograph with a DB-WAX column (30 m  $\times$  0.25 mm i.d.). Triplicate samples were taken out and analyzed after each time.

### High-Temperature Size-Exclusion Chromatography (HT-SEC)

A Waters 150C high-temperature SEC equipped with two PLgel 10  $\mu\text{m}$  mixed-B columns from Polymer Laboratories and an RI detector was used to measure changes in molecular weights



**Figure 2** Carbonyl index as a function of thermal aging time at 80°C in water and in air.

and distributions. The mobile phase was 1,2,4-trichlorobenzene (TCB) at 135°C and the flow rate was 1 mL/min. Calibration was performed according to polystyrene standards. Each sample was analyzed three times, and the molecular weight is given as an average of the values obtained.

#### Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was performed on a Perkin–Elmer 1760 Fourier transform infrared spectrometer with a 4x beam condenser. To use the attenuated total reflection technique (ATR) the instrument was equipped with a micro ATR holder and a KRS-5 prism with incident angle of 45°. On the IR spectra special interest was focused on the carbonyl region. Carbonyl absorbance at 1718  $\text{cm}^{-1}$  was measured relative to the  $\text{CH}_2$  scissoring peak at 1463  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

Figure 1 shows the number average molecular weights ( $M_n$ ), weight-average molecular weights ( $M_w$ ), and molecular weight distributions (MWD) of LDPE-MB, LDPE-starch, starch-EMA, and pure LDPE after thermal aging in air and water at 80°C. In air, the molecular weight of LDPE modified with starch and prooxidant formulation

in the form of masterbatch (LDPE-MB) decreased rapidly. At the same time MWD narrowed. During 11 weeks at 80°C in air no degradation was observed in the other materials (LDPE, LDPE-starch, and starch-EMA). During 11 weeks at 80°C in water all the materials, except LDPE-starch, decreased in molecular weight. The addition of small amount of starch, thus, made the material more stable than even pure LDPE towards the thermal degradation in water. The same phenomenon was also seen in a previous study of thicker films made of the same materials.<sup>18</sup> LDPE-MB degraded faster than the other materials even in water, but opposite to the starch-EMA and LDPE, the degradation of LDPE-MB proceeded faster in air than in water. Starch-EMA was resistant towards degradation in air, but it degraded almost as rapidly as LDPE-MB in water at 80°C.

During 11 weeks at 80°C in air the MWD of LDPE-MB decreased from 5.3 to 3.2. In water the MWD of LDPE-MB, starch-EMA, and LDPE instead broadened. The probability that two neighboring alkyl radicals will survive long enough to react with each other is increased by the lower oxygen concentration in water. These molecular enlargement reactions will broaden the molecular weight distribution. During the degradation in air there will be more available oxygen, and the probability that alkyl radicals will react with oxygen and form peroxy radicals instead of reacting with each other is increased.

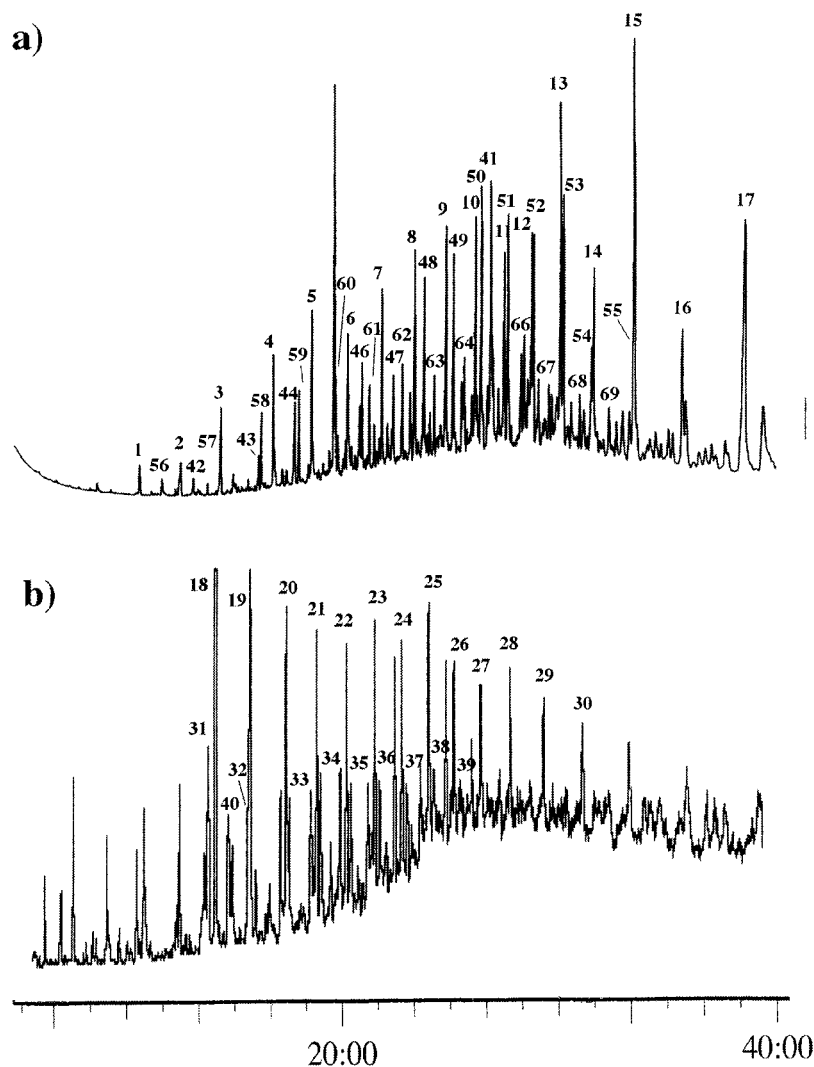
By FTIR, the extent of oxidation of polyethylene matrix was followed by monitoring the increase in carbonyl groups at the surface of the material. During the oxidation different carbonyl groups are formed in the polyethylene chain. These are acid groups at 1705  $\text{cm}^{-1}$ , ketones at 1718  $\text{cm}^{-1}$ , aldehydes at 1728  $\text{cm}^{-1}$ , the acyclic esters at 1740  $\text{cm}^{-1}$  and the cyclic esters at 1785  $\text{cm}^{-1}$ . Figure 2 shows the carbonyl absorbance of LDPE, LDPE-starch, and LDPE-MB after thermal aging in air and water measured at the maximum of the carbonyl peak at 1718  $\text{cm}^{-1}$ , i.e., the ketone group. Because starch-EMA was in the form of small granules instead of films, the carbonyl index of this material could not be measured by the ATR method. The number of carbonyl groups in LDPE-MB increased rapidly during the thermal aging in both environments, but the increase was faster in air than in water, in agreement with the molecular weight results. The molecular weight decrease and the increase in carbonyl index were fastest between 0 and 5 weeks and then leveled off in both environments. The

**Table I Degradation Products Formed in LDPE-MB during Different Aging Times at 80°C in Air**

	5 Weeks	11 Weeks		5 Weeks	11 Weeks
Carboxylic acids			41 benzoic acid	x	x
1 acetic acid	x				
2 propanoic acid	x		Hydrocarbons		
3 butanoic acid	x		42 hexadecane	x	x
4 pentanoic acid	x	x	43 heptadecane	x	x
5 hexanoic acid	x	x	44 octadecane	x	x
6 heptanoic acid	x	x	45 nonadecane	x	x
7 octanoic acid	x	x	46 eicosane	x	x
8 nonanoic acid	x	x	47 heneicosane	x	x
9 decanoic acid	x	x	48 docosane	x	
10 undecanoic acid	x	x	49 tricosane	x	
11 dodecanoic acid	x	x	50 tetracosane	x	
12 tridecanoic acid	x	x	51 pentacosane	x	
13 tetradecanoic acid	x	x	52 hexacosane	x	
14 pentadecanoic acid	x	x	53 heptacosane	x	
15 hexadecanoic acid	x	x	54 octacosane	x	
16 heptadecanoic acid	x	x	55 nonacosane	x	
17 octadecanoic acid	x	x			
			Ketones		
Dicarboxylic acids			56 2-decanone	x	x
18 butanedioic acid	x	x	57 2-undecanone	x	x
19 pentanedioic acid	x	x	58 2-dodecanone	x	x
20 hexanedioic acid	x	x	59 2-tridecanone	x	x
21 heptanedioic acid	x	x	60 2-tetradecanone	x	x
22 octanedioic acid	x	x	61 2-pentadecanone	x	x
23 nonanedioic acid	x	x	62 2-hexadecanone	x	x
24 decanedioic acid	x	x	63 2-heptadecanone	x	x
25 undecanedioic acid	x	x	64 2-octadecanone	x	x
26 dodecanedioic acid	x	x	65 2-nonadecanone	x	x
27 tridecanedioic acid	x	x	66 2-eicosanone	x	x
28 tetradecanedioic acid	x	x	67 2-heneicosanone	x	x
29 pentadecanedioic acid	x	x	68 2-docosanone	x	x
30 hexadecanedioic acid	x	x	69 2-tricosanone	x	x
Ketoacids					
31 4-oxopentanoic acid	x	x			
32 5-oxohexanoic acid	x	x			
33 6-oxoheptanoic acid	x	x			
34 7-oxooctanoic acid	x	x			
35 8-oxononanoic acid	x	x			
36 9-oxodecanoic acid	x	x			
37 10-oxoundecanoic acid	x	x			
38 11-oxododecanoic acid	x	x			
39 12-oxotridecanoic acid	x	x			
40 2-oxopentanedioic acid	x	x			

carbonyl index continued to increase in air between 5 and 11 weeks, but remained almost constant or decreased slightly in water. The MWD of LDPE-MB that initially broadened, narrowed slightly between 5 and 11 weeks in water. The dissolution of increasing amounts of low molecular weight carbonyl containing products (mono- and dicarboxylic acids) into water would both de-

crease the carbonyl index and narrow the MWD of the remaining films. LDPE-starch was more resistant towards thermal aging than the other materials and did not show any significant degradation in either environment. The carbonyl index of pure LDPE was constant in air, but increased between 5 and 11 weeks in water. These results parallel the molecular weight changes.



**Figure 3** GC-MS chromatogram of the products formed after 5 weeks of degradation of LDPE-MB in air at 80°C. (a) The hexane fraction with carboxylic acids, ketones, and alkanes; (b) the acidic methanol fraction with dicarboxylic acids and ketoacids. The numbered peaks are identified in Table I.

After 11 weeks in air the  $M_n$  of LDPE-MB had decreased to less than 25% of the initial value. This decrease in molecular weight was accompanied by a formation of large number of degradation products in various concentrations. Table I presents the degradation products identified in LDPE-MB after 5 and 11 weeks at 80°C in air. Figure 3 shows the GC-MS chromatograms of the products extracted from LDPE-MB after 5 weeks at 80°C in air. The main products in the chromatograms were carboxylic acids and benzoic acid in the hexane fraction and dicarboxylic acids in the methanol fraction. In addition, homologous series of alkanes, ketones, and ketoacids were identified. Trace amounts of *n*-alkanes and 1-alkenes were present already in the unaged samples. 1-Alkenes

were not detected after the thermal aging and were most likely further oxidized to other products like carboxylic acids during the aging. In accordance with the negligible molecular weight changes in the LDPE, LDPE-starch, and starch-EMA materials, no degradation products were detected in these materials.

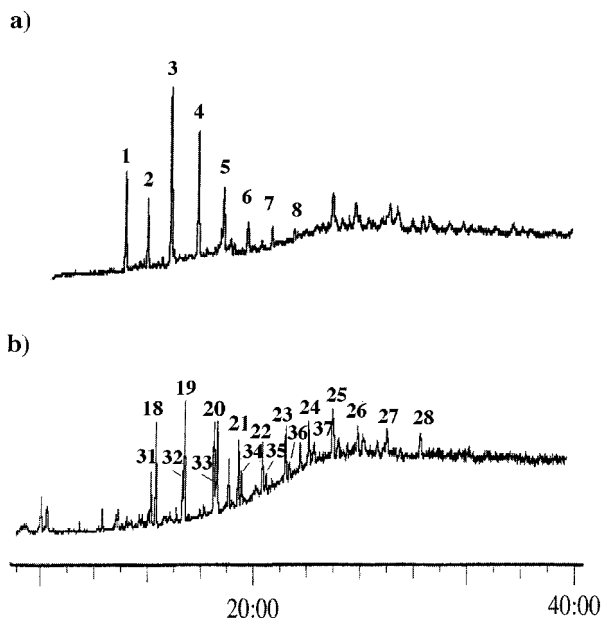
Table II gives the degradation products formed in LDPE, LDPE-MB, and starch-EMA in water at 80°C. LDPE-starch was the only material that did not form low molecular weight products during 11 weeks in water at 80°C, which is in agreement with the almost constant molecular weight and the negligible carbonyl group formation. The degradation products that leached out into the water phase during the aging were extracted with C18

**Table II Degradation Products Identified after Thermal Degredation of LDPE, LDPE-MB, and Starch-EMA at 80°C in Water**

	LDPE-MB		Starch-EMA		LDPE	
	5 Weeks	11 Weeks	5 Weeks	11 Weeks	5 Weeks	11 Weeks
<b>Carboxylic acids</b>						
1 acetic acid	x		x	x		x
2 propanoic acid	x					x
3 butanoic acid	x		x			x
4 pentanoic acid	x	x	x	x		x
5 hexanoic acid	x	x	x	x		x
6 heptanoic acid	x	x	x	x		x
7 octanoic acid	x	x	x	x		x
8 nonanoic acid	x	x	x	x		x
9 decanoic acid		x		x		
10 undecanoic acid		x				
11 dodecanoic acid		x				
12 tridecanoic acid		x				
13 tetradecanoic acid		x				
14 pentadecanoic acid		x				
15 hexadecanoic acid		x	x	x		
16 heptadecanoic acid		x				
17 octadecanoic acid	x	x		x		
<b>Dicarboxylic acids</b>						
18 butanedioic acid	x	x	x	x		x
19 pentanedioic acid	x	x	x	x		x
20 hexanedioic acid	x	x	x	x		x
21 heptanedioic acid	x	x	x	x		x
22 octanedioic acid	x	x	x	x		x
23 nonanedioic acid	x	x	x	x		x
24 decanedioic acid	x	x	x	x		x
25 undecanedioic acid	x	x	x	x		x
26 dodecanedioic acid	x	x	x	x		x
27 tridecanedioic acid	x	x		x		x
28 tetradecanedioic acid		x		x		x
29 pentadecanedioic acid				x		
30 hexadecanedioic acid				x		
<b>Ketoacids</b>						
31 4-oxopentanoic acid	x	x	x	x		x
32 5-oxohexanoic acid	x	x	x	x		x
33 6-oxoheptanoic acid	x	x		x		x
34 7-oxooctanoic acid	x	x	x	x		x
35 8-oxononanoic acid	x	x				x
36 9-oxodecanoic acid	x	x	x	x		x
37 10-oxoundecanoic acid	x	x				x
38 11-oxododecanoic acid	x	x				
39 12-oxotridecanoic acid	x	x				
40 2-oxopentanedioic acid	x	x		x		
41 benzoic acid	x	x				
70 lactic acid				x		
71 2-furancarboxaldehyde			x	x		

solid-phase extraction (SPE) columns. The products were separated and analyzed in two fractions (methanol and acidic methanol fractions). Figure 4 shows the two fractions extracted from pure

LDPE sample aged for 11 weeks in water. The same products were formed in all the materials after they had reached the same degree of degradation. The main products in the chromatograms



**Figure 4** GC-MS chromatogram of the products formed during 11 weeks of degradation of LDPE in water at 80°C. (a) the methanol fraction with carboxylic acids, and (b) the acidic methanol fraction with dicarboxylic acids and ketoacids. The numbered peaks are identified in Table II.

were identified as homologous series of mono- and dicarboxylic acids. In addition a homologous series of ketoacids was formed. Benzoic acid, earlier identified as a pyrolysis product from polystyrene,<sup>19</sup> was only identified in the degraded LDPE-MB samples. Benzoic acid is most likely a degradation product from the styrene part of the styrene-butadiene copolymer in the master batch formulation rather than a degradation product from polyethylene.

Mono- and dicarboxylic acids were the major products formed both in air and water, while ketones and hydrocarbons were only identified in air samples. Either these products are not formed in water or due to their nonpolar nature, they remain in the polymer matrix instead of migrating into the surrounding water. Two products, namely lactic acid and 2-furancarboxaldehyde, were only identified in the starch-EMA degraded in water at 80°C. 2-Furancarboxaldehyde has earlier been identified in pyrolyzed starch.<sup>20</sup> These products were not identified in any of the other materials, and they may be degradation products from starch.

LDPE-MB modified with starch and prooxidant was susceptible to degradation in air at 80°C in contrast to the other materials studied. The presence of prooxidant seems to be critical for the initi-

ation of degradation at moderate temperatures in dry air.<sup>3,7,11,21</sup> In water at 80°C the LDPE-MB films displayed longer degradation times than in air, although still faster than the other materials. In a previous study we could, by atomic absorption spectroscopy (AAS), show that the manganese contents of the LDPE-MB films decreased from the initial value of 68 ppm to less than 10 ppm during 30 weeks in water at 95°C.<sup>22</sup> The extraction of the transition metal salt from the polyethylene matrix by hot water may explain the slower degradation rate of LDPE-MB in water. In another study, LDPE films containing Co-acetylacetonate, Co-stearate, and Mn-stearate degraded rapidly in dry oven air at 60°C, while the degradation was much slower in compost.<sup>23</sup> After 8 weeks in the compost no further degradation was seen in the films during 5 days in an oven at 60°C. When the transition metal contents of LDPE films was measured by using X-ray fluorescence (XRF) Co-acetylacetonate was found to migrate out of the films during the composting, while the Mn-stearate remained in the films, but was somehow deactivated during the composting and could no longer initiate the degradation in dry oven, as observed by Weiland et al.<sup>23</sup>

## CONCLUSIONS

We have shown that LDPE-MB degraded rapidly at 80°C in air in contrast to the materials without prooxidants. The addition of prooxidants, thus, is essential for the degradation to proceed at moderate temperatures in air. LDPE-MB has the highest degradation rate both in air and water, but opposite to the other materials it is more susceptible to degradation in air than in water. The slower degradation rate in water is explained by the deactivation or leaching out of the prooxidant during the aging. The degradation of pure LDPE and starch-EMA is faster in water than in air. LDPE-starch was the only material that did not degrade during 11 weeks at 80°C in water, the addition of starch, thus made the material more stable than pure LDPE towards thermal aging in water. Mono- and dicarboxylic acids were the major products identified in both environments. Ketoacids were formed both in air and in water, while ketones were only detected after aging in air. Two products, namely lactic acid and 2-furancarboxaldehyde, were only identified in the starch-EMA degraded in water at 80°C. 2-Furancarboxaldehyde has earlier been identified in pyrolyzed starch. Lactic acid, on the other hand, is a well-



known fermentation product of glucose. The MWD of LDPE-MB narrowed during the aging in air, while MWD of LDPE-MB, starch-EMA, and LDPE broadened during the aging in water. The lower oxygen concentration in water increases the probability for molecular enlargement reactions compared to the degradation in air.

## REFERENCES

1. G. J. L. Griffin, U.S. Pat. 4,016,117 (1977).
2. G. J. L. Griffin, U.S. Pat. 4,021,388 (1977).
3. V. T. Breslin, *J. Environ. Polym. Degrad.*, **1**, 127 (1993).
4. H. B. Greizerstein, J. A. Syracuse, and P. J. Kostyniak, *Polym. Degrad. Stabil.*, **39**, 251 (1993).
5. V. T. Breslin and R. L. Swanson, *J. Air Waste Manage. Assoc.*, **43**, 325 (1993).
6. S. M. Goheen and R. P. Wool, *J. Appl. Polym. Sci.*, **42**, 2691 (1991).
7. W. Sung and Z. L. Nikolov, *Ind. Eng. Chem. Res.*, **31**, 2332 (1992).
8. G. J. L. Griffin, U.S. Pat. 4,983,651 (1991).
9. A.-C. Albertsson and S. Karlsson, *J. Appl. Polym. Sci.*, **35**, 1289 (1988).
10. K. E. Johnson, A. L. Pometto, III, L. Somasundaram, and J. Coats, *J. Environ. Polym. Degrad.*, **1**, 111 (1993).
11. A.-C. Albertsson, C. Barenstedt, and S. Karlsson, *Polym. Degrad. Stabil.*, **37**, 163 (1992).
12. A.-C. Albertsson, C. Barenstedt, and S. Karlsson, *J. Appl. Polym. Sci.*, **51**, 1097 (1994).
13. J. S. Peanasky, J. M. Long, and R. P. Wool, *J. Polym. Sci., Polym. Phys.*, **29**, 565 (1991).
14. A.-C. Albertsson, S. O. Andersson, and S. Karlsson, *Polym. Degrad. Stabil.*, **18**, 73 (1987).
15. A.-C. Albertsson, C. Barenstedt, T. Lindberg, and S. Karlsson, *Polymer*, **36**, 3075 (1995).
16. A.-C. Albertsson, C. Barenstedt, and S. Karlsson, *J. Chromatogr. A*, **690**, 207 (1995).
17. A.-C. Albertsson, C. Barenstedt, and S. Karlsson, *Acta Polym.*, **45**, 97 (1994).
18. B. Erlandsson, S. Karlsson, and A.-C. Albertsson, *Polym. Degrad. Stabil.*, to appear.
19. M. M. Shapi and A. Hesso, *J. Anal. Appl. Pyrol.*, **18**, 143 (1990).
20. D. J. Bryce and C. T. Greenwood, *Staerke*, **15**, 359 (1964).
21. K. E. Johnson, A. L. Pometto, III, and Z. L. Nikolov, *Appl. Environ. Microbiol.*, **59**, 1155 (1993).
22. C. Barenstedt, Ph.D. Thesis, Dept. Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden, 1994, p. 45.
23. M. Weiland and C. David, *Polym. Degrad. Stabil.*, **45**, 371 (1994).