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Solid-phase extraction and subsequent gas chromatography–mass spectrometry analysis for identification of complex mixtures of degradation products in starch-based polymers

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Abstract

A solid-phase extraction (SPE) method, using silica bonded with aminopropyl groups, was developed to separate highly complex mixtures of degradation products into three fractions. The SPE allowed the subsequent GC–MS identification of nearly 140 thermo-oxidation products of starch-based polymer blends, consisting of 70% starch and either ethylene maleic anhydride (EMA) or ethylene vinyl acetate maleic anhydride (EVAMA). It was thus possible to identify several homologous series of degradation products such as *n*-alkanes and 1-alkenes, 1-alcohols, 2-ketones, aldehydes, carboxylic acids and dicarboxylic acids. The homologous series of dicarboxylic acids ranged from butanedioic acid (C_4) to nonadecanedioic acid (C_{19}) and was for the first time identified in thermo-oxidized starch-based blends with polyethylene (PE). Hydrocarbons of even carbon number were formed to a larger extent than those with an uneven carbon number in the starch–EMA blend and the ratio *n*-alkane to 1-alkene increased (i.e. relatively more alkane is formed) under more severe thermo-oxidation conditions. The same phenomenon was not observed in the starch–EVAMA blend. Formic acid, acetic acid and γ-butyrolactone were the most predominant degradation products in both materials. Typical starch degradation products were difficult to resolve but we identified 2-hexanone, formic acid and acetic acid, which also have been reported previously to be degradation products of starch. The molecular mass measurements showed that the starch–EVAMA blend starts to degrade earlier than the starch–EMA, but on the other hand, at a lower rate. A good correlation between the decrease in M_n and the amount of degradation products formed was observed. A higher degree of cross-linking occurred in the starch–EVAMA blend in comparison with the starch–EMA blend and, in parallel, qualitatively and quantitatively more degradation products are formed in the starch–EMA blend.

Keywords: Solid-phase extraction; Polymers; Starch; Ethylene–vinyl acetate–maleic anhydride; Ethylene–maleic anhydride

1. Introduction

The low-molecular-mass compounds that are identified in degraded polymers are, in principle, related to synthesis, processing and/or use. Low-molecular-mass residuals and/or degradation products diffuse/migrate to the surrounding materials with potential toxicity and/or deleterious quality effects. Non-hydrolysable polymers, such as polyethylene, give rise to a complex pattern of degradation products, due to their random mode of degradation. In contrast, polymers with weak linkages, where specific degradation, like hydrolysis, occurs, generally give rise to a few, well-defined degradation products [1–4].

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We have studied pure low density polyethylene (LDPE) aged in aqueous media at different pH values and temperatures and identified a series of carboxylic acids, *n*-alkanes and alcohols [5]. In several papers we have presented and discussed the formation of degradation products focussing on the degradable polymers [2–4,6–8]. Recently it was possible for the first time to distinguish between abiotic and biotic degradation products in degradable LDPE [9].

The concept of chromatographic finger-printing in relation to polymers was presented by us in 1988. The biodegradation of casein gave rise to different degradation products depending on the type of microorganism responsible for the hydrolysis [1]. Recently we gave an overview of the degradation products of degradable polymers, where the correlation between the biodegradation mechanism of LDPE and the formed degradation products was presented [2]. Chromatographic finger-printing has thus been demonstrated as a method to differentiate between abiotic and biotic degradation of starch-filled degradable LDPE [2,9]. The microorganisms assimilate the low carboxylic acids formed during the degradation of the starch-filled LDPE and this is manifested as an absence of these carboxylic acids in the degradation product pattern obtained by GC–MS analysis. Furthermore, we demonstrated differences between abiotic and biotic degradation in the morphological behaviour. Starch-filled LDPE showed a decreasing value of crystallinity with prolonged ageing in a biotic environment, while the crystallinity of abiotically aged samples increased with prolonged degradation time [9].

Several thermo-oxidation studies in water and air identified abiotic degradation products of starch-filled degradable LDPE [6–8]. Traditional liquid–liquid extraction (LLE) allowed the subsequent identification of maybe 30–40 degradation products in the starch-filled LDPE, but the development of a solid-phase extraction (SPE) method allowed the identification of over 70 different degradation products [6]. SPE has in recent years gained in popularity due to its ability to selectively extract and isolate compounds of interest from various samples. The technique has found particular use in the selective extraction of steroids, lipids, peptides, drugs and pharmaceuticals from matrices such as plasma, blood, urine and culture media. Bonded phase sorbents of silica gel, with a wide variety of chemical functions, are commercially available.

This paper addresses fundamental issues involved in the analysis of degradation products of degradable polymers using starch-based polymers as models [starch–ethylene maleic anhydride (EMA) and starch–ethylene vinyl acetate maleic anhydride (EVAMA)]. It gives a detailed description of a new SPE that allows the separation of complex mixtures of degradation products before GC–MS identification. Correlation of the formed degradation products with the changes in molecular masses obtained by high-temperature size exclusion chromatography (SEC) is also presented.

2. Experimental

2.1. Materials

Two injection-molded blends were studied. Both materials contained 70 wt.% corn starch, blend I consisted of 30 wt.% of EMA and blend II consisted of 30 wt.% EVAMA. The vinyl acetate content in the EVAMA was 28%. The maleic acid content of EVAMA and EMA was approximately 0.8 mole%.

2.2. Thermo-oxidation

Polymer blends were thermally aged in air in closed glass vials (100 mg in each vial). Samples were degraded at 190°C (30 min or 3 h) and at 230°C (30 min).

2.3. SPE technique

After the thermal treatment, 0.5 ml of diethyl ether was added into the vials to extract the degradation products. After 1 h the diethyl ether was separated from the remaining polymeric material and evaporated to dryness with a gentle stream of nitrogen. The hexane-soluble products were dissolved in 1 ml of hexane and subjected to SPE. The remaining, hexane-insoluble, fraction was dissolved in 2% HCl in methanol (100 μl) and analysed separately. The SPE was developed and used to separate the products

into three fractions. The sorbent used for extraction was silica bonded to aminopropyl chains (NH_2) from Varian. The column was first activated with 2 ml of hexane. After activation, the hexane fraction, containing the degradation products, was passed through the column. The column was first washed with 1 ml of hexane, then with 1 ml of chloroform and finally with 2% acetic acid in diethyl ether (1 ml). The fractions were concentrated to 50 μl and subjected to GC–MS analysis. Fig. 1. shows the SPE method used in this work, which is a new version of a longer extraction scheme that was developed earlier by our group [6]. Unaged samples of both materials were also subjected to the same extraction procedure as a reference.

2.4. GC–MS

The gas chromatograph used was a Perkin Elmer 8500 Model with a split/splitless injector. It was connected to a Perkin Elmer ion-trap detector (ITD) mass spectrometer. The gas chromatograph was equipped with DB-1 (dimethyl polysiloxane) and DB-FFAP (nitroterephthalic acid modified polyethylene glycol) capillary columns from J & W (30 m×0.32 mm I.D.). The non-polar DB-1 column was used to analyse hexane, chloroform and methanol fractions with non-polar and medium polar degradation products. The polar DB-FFAP column, designed for the analysis of fatty acids, was used to analyse the ether–acetic acid fractions. The original ether fractions were analyzed with both columns. The column temperature was raised from 60°C to 325°C at 5°C/min for hexane fractions and from 40°C to 325°C at 5°C/min for chloroform and methanol fractions. The ether–acetic acid fraction was analysed with the DB-FFAP column that was programmed from 60°C to 250°C at 10°C/min and held at 250°C for 21 min. Helium was used as a carrier gas. The samples were introduced in the splitless injection mode at 250°C.

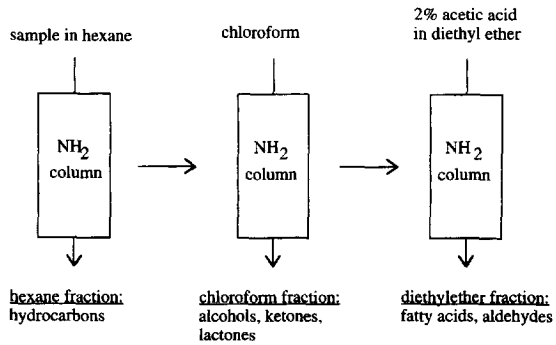


Fig. 1. The solid-phase extration method (SPE) for the isolation and separation of degradation products in starch–EMA and starch–EVAMA blends.

2.5. SEC

A Waters 150C high-temperature SEC apparatus, equipped with two PLgel 10 μm mixed-B columns and an RI detector, was used to measure changes in molecular masses 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 ranging between 770 000 g/mol and 2000 g/mol. The molecular masses obtained are thus only relative values.

3. Results

Oxidizable polymers form a series of low-molecular-mass compounds with varying polarity and volatility during degradation. It is not unusual to face the problem of identifying over a hundred products from e.g. polyethylene. The model polymers (i.e. starch–EMA and starch–EVAMA blends) also form many degradation products during ageing and it was therefore important to be able to adequately concentrate each individual fraction without risk of column overloading and also to reveal compounds of low concentration. A SPE scheme was developed in this context.

Fig. 1 shows the SPE scheme; diethyl ether was first added to the sample vials and the products were allowed to diffuse out from the polymer matrix for 1 h. Thereafter, the remaining polymer was separated from the diethyl ether fraction, which was evaporated to dryness. The hexane-soluble products were then separated from the insoluble fraction which was dissolved in 2% HCl in methanol. The hexane-soluble fraction passed through the SPE column according to Fig. 1 (see Section 2 for detailed

information). The resulting three fractions were analysed by GC–MS.

The molecular mass changes and distributions are given in Table 1. Initially, the M_n of the starch–EVAMA blend decreased more than that of starch–EMA. Degradation time and/or degradation temperature influence the value of the M_n decrease, e.g. the M_n of starch–EMA decreased faster at higher temperature or longer degradation time than the M_n of starch–EVAMA. The M_z-value was almost constant during the degradation for starch–EMA, which was not the case for the starch–EVAMA samples. This is indicative of a larger degree of cross-linking in this material. The starch–EMA is more susceptible to thermo-oxidation and it shows less tendency to cross-link than the starch–EVAMA samples.

The molecular mass changes correlate well with the result of the GC–MS analysis of degradation products. Both type of blends form complex patterns of low-molecular-mass compounds during thermo-oxidation. Fig. 2 shows some examples of the gas chromatograms of the thermo-oxidation products of starch–EVAMA and starch–EMA blends obtained by direct analysis of the diethyl ether fractions without the SPE procedure. The most abundant compounds identified are formic acid, acetic acid and, at 230°C, γ-butyrolactone. The thermo-oxidized starch–EVAMA blend formed considerably more acetic acid than did the starch–EMA blend. Increased ageing temperature from 190°C to 230°C during the same period of time causes changes in both the type and the amount of oxidation products. Less than 40 products were identified after 30 min at 190°C, compared to 138 products at 230°C. The compounds belong to the groups hydrocarbons, alcohols, ketones, aldehydes, lactones, acids and diacids.

Fig. 3a–c and Fig. 4 b show the degradation products of starch–EMA (aged for 0.5 h at 230°C) isolated and separated by the SPE method and subsequently identified by GC–MS. In the hexane fraction, hydrocarbons where identified ranging from octane to 1-octacosene. The chloroform fraction contained alcohols from 1-pentanol to 1-docosanol and ketones from 2-pentanone to 2-docosanone. The diethyl ether fraction revealed several different carboxylic acids and aldehydes, while the methanol phase (from the hexane-insoluble phase not subjected to SPE) contained dicarboxylic acids ranging in length from butanedioic acid to nonadecanedioic acid.

Table 2 gives all the identified thermo-oxidation products and the relative amount of each compound. It should be taken into consideration that the response factor is not the same for all compounds and that losses occur during the extraction steps due to volatility and/or non-quantitative recoveries from the SPE columns.

3.1. Starch–EMA.

After 30 min at 190°C, only a few products were formed. After 3 h at 190°C the number of products formed had increased considerably. After thermo-oxidation at 230°C, the same products (but in different amounts) were identified predominantly. γ-Butyrolactone became the most abundant product at 230°C, together with formic acid and acetic acid, as seen in Fig. 2. In the fraction from SPE and the

Table 1
Molecular mass changes during thermo-oxidation of starch–EMA and starch–EVAMA, as obtained by HT-SEC

		M_n	M_w	M_z	M_w/M_n
Starch–EMA	Unaged	20 524	92 375	280 545	4.5
	0.5 h at 190°C	19 723	78 902	258 186	4.0
	3 h at 190°C	4 695	62 086	294 543	13.2
	0.5 h at 230°C	5 160	62 916	267 267	12.2
Starch–EVAMA	Unaged	23 297	126 076	499 755	5.4
	0.5 h at 190°C	17 447	157 258	809 155	9.0
	3 h at 190°C	8 121	90 671	432 469	11.2
	0.5 h at 230°C	13 987	142 018	791 066	10.2

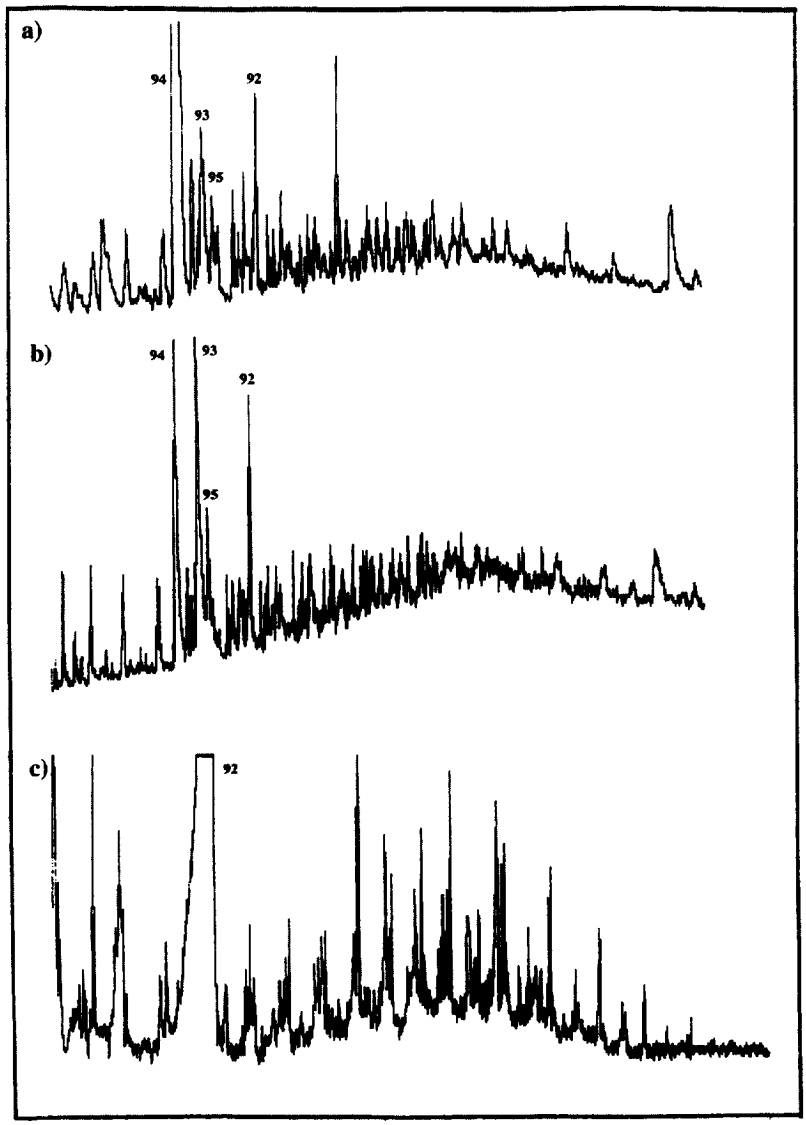


Fig. 2. Ion chromatograms of degradation products formed in starch–EMA and starch–EVAMA aged at 230°C for different periods of time. The products were extracted with diethyl ether. (a) Starch–EVAMA after 0.5 h, GC–MS with DB-FFAP column; (b) starch–EMA after 0.5 h, GC–MS with DB-FFAP column and (c) starch–EMA after 0.5 h, GC–MS analysis with DB-1 column. DB-FFAP column is especially suited for polar compounds (e.g. carboxylic acids), while DB-1 is suitable for non-polar compounds.

HCl–methanol fraction, a few short chain alcohols, ketones and dicarboxylic acids were also identified, in addition to hydrocarbons.

Fig. 4 gives examples of chromatograms of the SPE hexane fraction that contain the hydrocarbon formed in the two thermo-oxidized blends. Fig. 4b–d show the hydrocarbons in the starch–EMA blend. In particular *n*-alkanes and 1-alkenes with an even number of carbon atoms were identified (Fig. 4c). The same hydrocarbons were present in the hexane fraction of unaged samples but in smaller amounts.

We have also successfully identified several

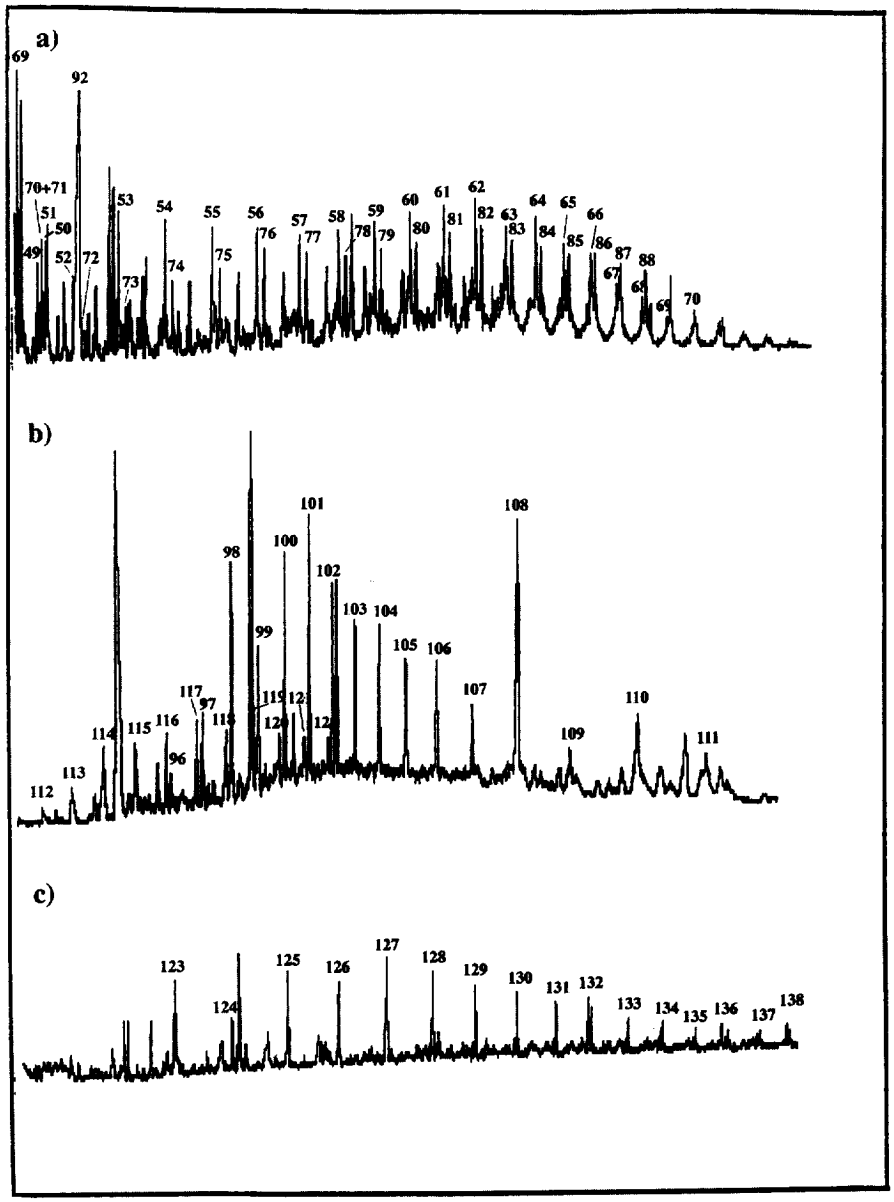


Fig. 3. Ion chromatograms of the SPE fractions and the hexane-insoluble fraction (dissolved in methanol). Starch–EMA thermo-oxidized at 230°C for 0.5 h. (a) Chloroform fraction, GC–MS analysis with DB-1 column; (b) diethyl ether fraction, GC–MS analysis with DB-FFAP column and (c) methanol fraction, GC–MS analysis with DB-1 column. DB–FFAP column is especially suited for polar compounds (e.g. carboxylic acids), while DB-1 is suitable for non-polar compounds.

homologous series such as the *n*-alkanes and 1-alkenes in the hexane fraction (Fig. 4b–d), 1-alcohols, 2-ketones in the chloroform fraction (Fig. 3a), aldehydes and carboxylic acids in the diethyl ether fraction (Fig. 3b) and dicarboxylic acids in the methanol fraction (Fig. 3c). In addition 2- and 3-hexanol, 3-hexanone and γ-butyrolactone were identified. γ-Butyrolactone was in fact the major product in the chloroform fraction from the starch–EMA blend.

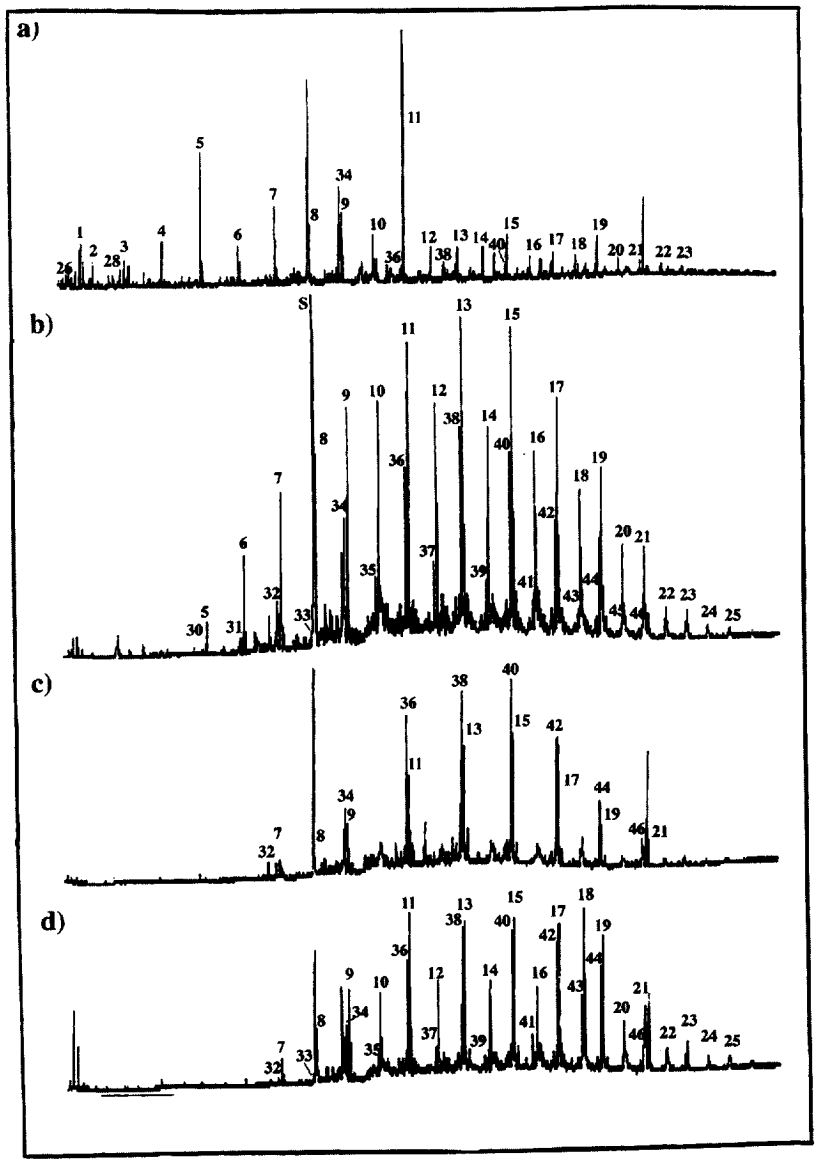


Fig. 4. Ion chromatograms of hexane fractions obtained after SPE isolation. (a) Starch–EVAMA at 230°C for 0.5 h; (b) starch–EMA at 230°C for 0.5 h; (c) starch–EMA at 190°C for 0.5 h; (d) starch–EMA at 190°C for 3 h. All hexane fractions were analyzed by GC–MS with a DB-1 column.

3.2. Starch–EVAMA

Acetic acid was by far the most abundant product after thermal degradation of starch–EVAMA (Fig. 2a). Even after 30 min at 190°C, when only a few other products were detected, some acetic acid was formed. Otherwise, mainly the same products were identified in starch–EVAMA as in thermo-oxidized starch–EMA, but in smaller amounts. In contrast with the hydrocarbons found in starch–EMA, only small amounts of *n*-alkanes and almost no 1-alkenes were formed after thermal degradation of the starch–EVAMA blend (Fig. 4a). There was no clear preference for formation of hydrocarbons with an even

Table 2
Identified compounds and their relative amounts in starch–EMA and starch–EVAMA aged at 190°C and 230°C for 0.5 and 3 h. A majority of the identified compounds were isolated and separated by SPE before GC–MS analysis. The amount of formic acid and acetic acid was calculated before SPE, otherwise the calculation would relate to the peak obtained after SPE separation

	Compound	t_R	Starch–EMA				Starch–EVAMA			
	(Hexane fraction)		Unaged	190°C 0.5 h	190°C 3 h	230°C 0.5 h	Unaged	190°C 0.5 h	190°C 3 h	230°C 0.5 h
	Hydrocarbons									
1	Octane	5.5							2	3
2	Nonane	7.3							2	3
3	Decane	10				1		0.5	3	5
4	Undecane	12.5				1		3	10	8
5	Dodecane	15.5				6		4	10	25
6	Tridecane	18.4				20		2	6	8
7	Tetradecane	21.3		2	4	34		4	9	16
8	Pentadecane	24.1	0.5	1	6	39	1	6	6	11
9	Hexadecane	26.4	3	6	15	53	4	6	10	15
10	Heptadecane	29			13	49	4	5	8	13
11	Octadecane	31.2	6	12	27	68	5	3	5	91
12	Nonadecane	33.3			15	52	4	2	4	6
13	Eicosane	35.4	4	14	29	69	2	1	4	6
14	Heneicosane	37.4			14	46	1	1	3	7
15	Docosane	39.3	3	16	28	67	0.5	1	3	9
16	Tricosane	41.2			11	42	0.5	1	5	5
17	Tetracosane	43.1	2	10	24	53		0.5	1	6
18	Pentacosane	44.5			36	30		0.5	1	4
19	Hexacosane	46.3	1	6	18	34		0.5	1	8
20	Heptacosane	48.1			6	16			0.5	4
21	Octacosane	49.5	1	3	13	21				3
22	Nonacosane	51.2			8	12				3
23	Triacontane	52.5			3	46				2
24	Heneitriacontane	54.3			4	44				
25	Dotriacontane	56.1			3	29				
26	1-Octene	5.4							2	2
27	1-Nonene	7.2							1	1
28	1-Decene	9.4							4	3
29	1-Undecene	12.4								
30	1-Dodecene	15.3	0.5			1				
31	1-Tridecene	18.2				4				
32	1-Tetradecene	21.1		2	1	8				
33	1-Pentadecene	24			1	4				
34	1-Hexadecene	26.3	4	9	8	22				20
35	1-Heptadecene	28.5			3	10				
36	1-Octadecene	31.1	8	18	19	37				19
37	1-Nonadecene	33.2			4	13				
38	1-Eicosene	35.3	9	25	28	43			1	2
39	1-Heneicosene	37.3			3	10				
40	1-Docosene	39.2	6	26	27	41			1	3
41	1-Tricosene	41.1			2	6				2
42	1-Tetracosene	43.1	5	18	24	28				2
43	1-Pentacosene	44.4			11	4				1
44	1-Hexacosene	46.2	3	10	15	17				
45	1-Heptacosene	48				0.5				
46	1-Octacosene	49.4	2	4	10	5				
47	1-Nonacosene	51.1								
48	1-Triacontene	52.4			4					

Table 2 (Continued)

	Compound	t_R	Starch–EMA				Starch–EVAMA			
	(Chloroform fraction)		Unaged	190°C 0.5 h	190°C 3 h	230°C 0.5 h	Unaged	190°C 0.5 h	190°C 3 h	230°C 0.5 h
	Alcohols									
49	1-Pentanol	6.2		0.5	3	15		0.5	4	10
50	3-Hexanol	7		2	4	10		3	5	5
51	2-Hexanol	7.1		4	7	14		5	7	8
52	1-Hexanol	8.5			4	8		0.5	2	6
53	1-Heptanol	11.5		2	7	30		2	5	18
54	1-Octanol	15.1			6	23		1	4	11
55	1-Nonanol	18.2			7	32		0.5	3	11
56	1-Decanol	21.2			8	35			1	6
57	1-Undecanol	24.2			14	34			2	10
58	1-Dodecanol	27.1			8	32				13
59	1-Tridecanol	29.4			6	27				4
60	1-Tetradecanol	32.1			4	28				3
61	1-Pentadecanol	34.3			9	31				6
62	1-Hexadecanol	36.5			11	26				10
63	1-Heptadecanol	39			8	21				3
64	1-Octadecanol	41			20	24				10
65	1-Nonadecanol	43			18	20				6
66	1-Eicosanol	44.5				7				
67	1-Heneicosanol	46.4				7				
68	1-Docosanol	48.3				6				
	Ketones									
69	2-Pentanone	5.1		24	8	51		28	27	22
70	3-Hexanone	6.4			4	12		6	7	8
71	2-Hexanone	6.5		8	12	21		10	14	20
72	2-Heptanone	9.2		0.5	6	7			3	4
73	2-Octanone	12.2			8	16			3	4
74	2-Nonanone	15.4			8	20		0.5	4	5
75	2-Decanone	18.5		1	10	31		0.5	3	6
76	2-Undecanone	22			10	30		1	4	9
77	2-Dodecanone	24.5			12	53		0.5	3	6
78	2-Tridecanone	27.3		0.5	18	28			7	15
79	2-Tetradecanone	30.1			14	26			3	6
80	2-Pentadecanone	32.4			15	27		0.5	3	5
81	2-Hexadecanone	35			20	29			4	6
82	2-Heptadecanone	37.1			12	22			4	5
83	2-Octadecanone	39.2			12	19			3	5
84	2-Nonadecanone	41.2			13	18			3	4
85	2-Eicosanone	43.2			8	15			9	5
86	2-Heneicosanone	47			9	8			4	
87	2-Docosanone	48.4			13	19				
88	2-Tricosanone	50.3								
89	2-Tetracosanone	52.1								
90	2-Pentacosanone	53.4								
91	2-Hexacosanone	55.2								
	Lactones									
92	Butyrolactone	9.1			65	157			41	93

Table 2 (Continued)

	Compound	t_R	Starch–EMA				Starch–EVAMA			
	(Ether fraction)		Unaged	190°C 0.5 h	190°C 3 h	230°C 0.5 h	Unaged	190°C 0.5 h	190°C 3 h	230°C 0.5 h
	Acids									
93	Formic acid (a)	10.2			113	157			79	21
94	Acetic acid (a)	9.3			98	104		33	329	635
95	Propanoic acid	10.4			24	27			26	42
96	Butanoic acid	11.5			4	12			35	26
97	Pentanoic acid	13.2			5	36			42	28
98	Hexanoic acid	14.4			26	89			46	32
99	Heptanoic acid	15.5			28	46			23	20
100	Octanoic acid	17			33	76			19	27
101	Nonanoic acid	18.1			57	85			30	22
102	Decanoic acid	19.2			26	63			15	7
103	*n*-Hendecanoic acid	20.2			29	60			12	10
104	Dodecanoic acid	21.3			62	64			23	10
105	Tridecanoic acid	22.5			26	55			8	9
106	Tetradecanoic acid	24.1			34	58			17	11
107	Pentadecanoic acid	25.5			28	35				6
108	Hexadecanoic acid	28			65	187			35	3
109	Heptadecanoic acid	30.3			20					
110	Octadecanoic acid	33.4			45					
111	Nonadecanoic acid	36.5			46					
	Aldehydes									
112	Heptanal	6			22	10				
113	Octanal	7.2			4	28				
114	Nonanal	8.5			28	58				
115	Decanal	10.2			3	39				
116	Undecanal	11.4			1	32			3	3
117	Dodecanal	13			2	34			4	4
118	Tridecanal	14.2			1	36			3	3
119	Tetradecanal	15.4				16			4	
120	Pentadecanal	16.5				12			4	3
121	Hexadecanal	18				16				
122	Heptadecanal	19.1				8				
	(Methanol fraction)									
	Diacids									
123	Butanedioic acid	13.3			52	22		2	25	14
124	Pentanedioic acid	16.4		1	40	15		2	25	8
125	Hexanedioic acid	19.4		2	31	22		3	35	10
126	Heptanedioic acid	22.5		1	29	22		3	31	9
127	Octanedioc acid	25.4		2	38	21		1	35	8
128	Nonanedioic acid	28.2		0.5	37	20		2	20	8
129	Decanedioic acid	30.5		0.5	30	17		1	17	6
130	Undecanedioic acid	33.1		0.5	24	15		1	16	5
131	Dodecanedioic acid	35.3		0.5	22	14		1	14	4
132	Tridecanedioic acid	37.4			18	9			11	3
133	Tetradecanedioic acid	39.5			14	10			2	6
134	Pentadecanedioic acid	41.5			18	9			9	5
135	Hexadecanedioic acid	43.4			15	7			7	3
136	Heptadecanedioic acid	45.3			16	6			4	2
137	Octadecanedioic acid	47.2			12	4			3	
138	Nonadecanedioic acid	49			11					

carbon number, as was the case for the starch–EMA. The formation of dodecane, octadecane, 1-hexadecene and 1-octadecene was favoured at 230°C. The most abundant product classes were otherwise mono- and dicarboxylic acids (Fig. 2a, Fig. 4a).

4. Discussion

The type of degradation products identified in the two blends belong to the same groups, but the amount of the individual compounds differ between the two materials. A good correlation between a low value of M_n and a large amount of formed degradation products is observed for the starch–EMA blend, which is the reverse of the starch–EVAMA case. Earlier studies have established the thermal degradation products of polyethylene (PE) [10–18], polyvinyl acetate (PVAc) [19–22] and starch [23,24].

At this stage, correlation of the degradation products with the different components of the blends is difficult. 2-hexanone, formic acid and acetic acid could, for example, be thermal degradation products of starch [23,24], although thermal degradation of starch has been reported to lead exclusively to depolymerization unless the temperature applied exceeds 300°C [23]. The amount of γ-butyrolactone increased substantially when the temperature or the heating time were increased and it became one of the major products at 230°C. This agrees well with other results from our group [6,7], which showed that γ-lactones are mainly formed during more severe oxidation of PE. The formation of γ-lactones can occur whenever carboxylic acid and hydroxyl groups are generated in the 1,4-positions of the polymer backbone [16]. The decomposition of 1,4-dihydroxyperoxides [25] and/or the homolysis of a percarboxyl group [15] are other possible mechanisms giving γ-butyrolactone.

The large amount of acetic acid formed in the degraded starch–EVAMA blend is related to the vinyl acetate part, which constitutes 28% of the EVAMA component. Formic acid and acetic acid were otherwise the major degradation products detected for both materials. The formation of large amounts of formic acid and acetic acid after thermal oxidation of PE was described for the first time in an early work by Bevilacqua et al. [26]. More acetic acid is formed during the degradation of starch–EVAMA than in pure PE, which is due to deacetylation of the acetate groups in the vinyl acetate part of the blend.

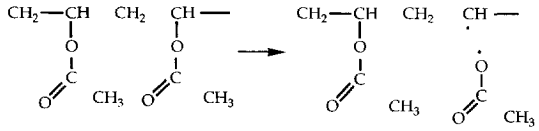
The earliest significant work on thermal degradation of PVAc was carried out by Grant and Grassie [19–21]. They established that, on heating, the polymer loses acetic acid in a nearly quantitative yield of one acetic acid molecule per original monomer unit. They also found that acetic acid accounted for up to 95% of the evolved volatiles during degradation at 213–235°C. They suggested that the thermal cleavage of the C–OAc bond occurs by way of a six-membered ring transition state:

A hydrogen atom is abstracted from the adjacent methylene group. Once a double bond is formed, the next and succeeding acetoxy groups are more reactive due to the allylic structure, and thus an unzipping chain reaction is initiated.

The thermal degradation of PVAc and its blends have been the subject of several reports [18,27–32]. All agreed that the main volatile product (90% or more) of the thermal degradation of PVAc is acetic acid. Other products that have been identified are carbon dioxide, carbon monoxide, water and a ketene. The kinetic curve for PVAc deacetylation has a distinct autocatalytic character and rapid cross-linking of the polymer takes place. This agrees with our results, where the increasing value of M_w and M_z for the starch–EVAMA indicate that cross-linking takes place (Table 1).

In another study, we used headspace-GC–MS to identify volatile degradation products of starch–EMA and starch–EVAMA at 150°C [33]. The major degradation products identified were formic acid and acetic acid. In the starch–EMA blend, products were not formed until after 3 h degradation at 150°C. On the other hand, the starch–EVAMA blend formed a considerable amount of acetic acid, even after 15 min at 150°C. This agrees well with the SEC results, where the molecular masses of starch–EVAMA decrease earlier than that of starch–EMA. This is explained if we assume that the degradation reaction

in EVAMA involves, as the first step, the homolysis of the C–O bond that attaches the acetate group to the polymer backbone:



The small radicals that are formed abstract a hydrogen atom from the ethylene part, instead of the β-hydrogen from the vinyl acetate, thus triggering the degradation. This homolysis, instead of being a simple molecular elimination of acetic acid, provides a ready explanation for the cross-linking process, through reactions of pairs of macroradicals.

Fig. 4a–d shows examples of the hydrocarbons formed in the starch–EMA and starch–EVAMA blends after thermo-oxidation. In a starch–EMA blend, the hydrocarbons with even carbon numbers were always more abundant than those with an uneven carbon number. This is explained by the higher energy required for the dissociation into C_1 and C_{2x-1}, where every other C–C bond that is not in the α-position to one chain end is assumed to have an almost equal dissociation energy [34]. In support of this, it is generally observed that thermal degradation of poly(α-olefins) rarely results in the separation of methane from chain and branch ends and from tertiary or quarternary carbon atoms [35]. In the case of starch–EVAMA, however, no preference for the formation of hydrocarbons with even carbon numbers could be seen. Hydrocarbons are formed by simple chain cleavage from the polyethylene. Copolymers of ethylene and vinyl acetate are usually believed to be random, because of the similarity in the ethylene and vinyl acetate reactivity ratios. This random structure probably disturbs the formation of hydrocarbons. Unsaturated hydrocarbons may be further oxidized more easily than saturated ones and this explains why, under more severe thermo-oxidation conditions, the amount of both *n*-alkanes and 1-alkenes increased but the relative amount of 1-alkenes compared to *n*-alkanes decreased.

We also report the identification of a series of dicarboxylic acids in these starch blends (Table 2). This was achieved by improving the chromatographic behaviour by methylation of the dicarboxylic acids with acidic methanol to the subsequent dimethyl esters. The dicarboxylic acids can be formed according to the mechanisms for the monocarboxylic acid formation involving a dual β-cleavage of alkoxy radicals. We have, in earlier work, identified dicarboxylic acids also in starch-filled degradable LDPE samples that were degraded in water at 95°C for 30 weeks [6]. The formation of these acids was also previously described as degradation products of PE subjected to boiling nitric acid [15].

5. Conclusions

A convenient SPE method for the separation of complex mixtures of degradation products has been developed. This SPE method is based on solid sorbents of bonded silica of the aminopropyl type. Application of the method to thermo-oxidative degradation products of starch blends (i.e. starch–EVAMA and starch–EMA) allowed the separation of 140 different compounds into four fractions. The resulting GC–MS chromatograms gave a more detailed description of the complex degradation product mixtures. Hydrocarbons (alkane and alkene), alcohols, ketones, lactones, carboxylic acids, aldehydes and dicarboxylic acids were identified in varying amounts and patterns in the two starch blends. Large amounts of acetic acid, formic acid and γ-butyrolactone were formed in both types of material. Increasing the temperature from 190°C to 230°C resulted in γ-butyrolactone being the most abundant compound, especially in the starch–EMA blend. We also demonstrate a preference for forming hydrocarbons with an even, rather than an uneven, carbon number in the degraded starch–EMA blend. In the starch–EMA blend, we also found that the lower temperature (190°C) favoured the formation of alkene while the higher temperature (230°C) favoured the formation of more alkane. These two phenomena were not seen in the starch–EVAMA blend.

References

[1] S. Karlsson, Z.G. Banhidi and A.-C. Albertsson, J. Chromatogr., 442 (1988) 267.

[2] S. Karlsson and A.-C. Albertsson, J. Macromol. Sci. Pure Appl. Chem., A32 (1995) 599.
[3] S. Karlsson, M. Hakkarainen and A.-C. Albertsson, J. Chromatogr. A, 688 (1994) 251.
[4] S. Karlsson, C. Sares, R. Renstad and A.-C. Albertsson, J. Chromatogr. A, 669 (1994) 97.
[5] A.-C. Albertsson and S. Karlsson, in G. Glass and G. Swift (Editors), Agricultural and Synthetic Polymers, ACS Symposium Series No. 433, Am. Chem. Soc., Washington, DC, 1990, p. 60.
[6] A.-C. Albertsson, C. Barenstedt and S. Karlsson, J. Chromatogr. A, 690 (1995) 207.
[7] A.-C. Albertsson, C. Barenstedt and S. Karlsson, Acta Polymerica, 45 (1994) 97.
[8] A.-C. Albertsson, C. Barenstedt and S. Karlsson, Polym. Degrad. Stab., 37 (1992) 163.
[9] A.-C. Albertsson, C. Barenstedt, T. Lindberg and S. Karlsson, Polymer, 36 (1995) 3075.
[10] S. Morisaki, Thermochimica Acta, 9 (1974) 157.
[11] J. Michal, J. Mitera and S. Tardon, Fire and Materials, 1 (1976) 160.
[12] A. Hoff and S. Jacobsson, J. Appl. Polym. Sci., 26 (1981) 3409.
[13] A. Bravo and J.H. Hotchkiss, J. Appl. Polym. Sci., 47 (1993) 1741.
[14] V. Pacakova, P.A. Leclercq, S. Holotik and I. Beroum, Anal. Lett., 18 (1985) 1759.
[15] M. Iring, F. Tudös, Zs. Fodor and T. Kelen, Polym. Degrad. Stab., 2 (1980) 143.
[16] J. Lacoste, D.J. Carlsson, S. Falicki and D.M. Wiles, Polym. Degrad. Stab., 34 (1991) 309.
[17] M. Iring and F. Tudös, Prog. Polym. Sci., 15 (1990) 217.
[18] A. Jamieson and I.C. McNeill, J. Polym. Sci., Polym. Chem. Ed., 14 (1976) 1839.
[19] D.H. Grant and N. Grassie, Trans. Faraday Soc., 48 (1952) 379.
[20] D.H. Grant and N. Grassie, Trans. Faraday Soc., 56 (1960) 445.
[21] N. Grassie, Trans. Faraday Soc., 49 (1953) 835.
[22] D.L. Gardner and I.C. McNeill, J. Thermal. Anal., 1 (1969) 389.
[23] P. Tomasik, S. Wiejak and M. Palanski, Adv. Carbohyd. Chem. Biochem., 47 (1989) 279.
[24] V.G. Kumar, M.V. Bhandary and A.N. Bhat, Thermochim. Acta, 146 (1989) 201.
[25] J. Lacoste, R. Arnaud, P. Singh and J. Lemaire, Makromol. Chem., 189 (1988) 651.
[26] E.M. Bevilacqua, E.S. English and J.S. Gall, J. Appl. Polym. Sci., 8 (1964) 1691.
[27] I.C. McNeill, A.Y. Polishchuk and G.E. Zaikov, Polym. Degrad. Stab., 37 (1992) 223.
[28] E.M. Barrall, II, R.S. Porter and J.F. Johnson, Anal. Chem., 35 (1963) 73.
[29] B.B. Troitskii, G.A. Razuvaev, L.V. Khokhlova and G.N. Bortnikov, J. Polym. Sci., 42 (1973) 1363.
[30] I.K. Varma and R.K. Sadhir, Angew. Macromol. Chem., 46 (1975) 1.
[31] A. Jamieson and I.C. McNeill, J. Polym. Sci., Polym. Chem. Ed., 14 (1976) 603.
[32] C. Caze and C. Loucheux, J. Macromol. Sci.-Chem., A15 (1981) 95.
[33] D. Ramkumar, U.R. Vaidya, M. Bhattacharya, M. Hakkarainen, A.-C. Albertsson and S. Karlsson, Eur. Polym. J., (1996) in press.
[34] M. Seeger and R.J. Gritter, J. Polym. Sci., Polym. Chem. Ed., 15 (1977) 1393.
[35] M. Seeger and H.-J. Cantow, Makromol. Chem., 176 (1975) 2059.