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Development of a solid-phase extraction method for simultaneous extraction of adipic acid, succinic acid and 1,4-butanediol formed during hydrolysis of poly(butylene adipate) and poly(butylene succinate)

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Abstract

A solid-phase extraction (SPE) method was developed for the simultaneous extraction of dicarboxylic acids and diols formed during hydrolysis of poly(butylene succinate), PBS, and poly(butylene adipate), PBA. Four commercial non-polar SPE columns, three silica based: C_8, C_{18}, C_{18} (EC), and one resin based: ENV+, were tested for the extraction of succinic acid, adipic acid and 1,4-butanediol, the expected final hydrolysis products of PBS and PBA. ENV+ resin was chosen as a solid-phase, because it displayed the best extraction efficiency for 1,4-butanediol and succinic acid. Linear range for the extracted analytes was 1–500 ng/μl for adipic acid and 2–500 ng/μl for 1,4-butanediol and succinic acid. Detection and quantification limits for the analytes were between 1–2 and 2–7 ng/μl, respectively, and relative standard deviations were between 3 and 7%. Good repeatability and low detection limits made the developed SPE method and subsequent gas chromatography–mass spectrometry (GC–MS) analysis a sensitive tool for identification and quantification of hydrolysis products at early stages of degradation.

Keywords: Adipic acid; Succinic acid; Organic acids; Butanediol; Poly(butylene adipate); Poly(butylene succinate)

1. Introduction

The analysis of low-molecular-mass degradation products released from polymers is important both to protect people dealing with plastic products and the environment around us. In the case of degradable polymers, degradation process and intermediate and final degradation products should be elucidated quantitatively, to evaluate the environmental adaptability of the material. In addition, degradation products provide information about the degradation procedure and mechanisms. Gas chromatography–mass spectrometry (GC–MS) together with appropriate extraction method is a sensitive tool for detecting early signs of degradation in the material, e.g. solid phase microextraction and GC–MS analysis of the degradation products showed oxidation-induced changes in recycled and thermo-oxidized polyamide 66 considerably earlier than tensile testing, FTIR or DSC [1,2]. The amount and type of degradation products formed was also in good correlation with the degree of degradation in the polymer matrix [2–4]. Among other methods used to analyze polar degradation products from polymers, HPLC in combination with atmospheric pressure chemical ionization mass spectrometry (APCI-MS) and electrospray ionization mass spectrometry (ESI-MS) can be mentioned [5].

When aliphatic polyesters are hydrolyzed, usually merely a few degradation products are formed. However, depending of the structure of the polyester and the environment it is subjected to, the time for degradation/fragmentation of the material can vary from days to several years. In addition to the chemical structure, many factors influence the hydrolysis rate including macromolecular architecture, molecular weight, crystallinity, morphology, the presence of impurities and residual monomers, degradation media, etc. The usual degradation products formed in abiotic aqueous environments are hydroxyacids, dicarboxylic acids, diols and different oligomeric species formed by simple hydrolysis of

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ester bonds [6–9]. Acidic end-groups autocatalyze continued degradation [10,11] and water-soluble oligomers degrade to monomers if hydrolysis is allowed to continue [7]. During biotic degradation, oligomers and monomers are frequently formed as intermediate degradation products [12–22]. These products should then be assimilated and metabolized by microorganisms [16–18]. This may lead to formation of other intermediate degradation products, e.g. acetic acid and propanoic acid, known fermantation products of lactic acid, were detected when poly(L-lactide) (PLLA) was aged in mineral medium inoculated with compost microorganisms [17]. The amount of lactic acid steadily increased during abiotic hydrolysis of PLLA, while the amount detected during biotic hydrolysis remained low due to assimilation of formed lactic acid by microorganisms [18]. The amount of easily assimilated lactic acid and lactoyl lactic acid in the PLLA films also enhanced the degradation rate in biotic medium [17].

Short-chain dicarboxylic acids and diols have earlier been extracted by sequential liquid–liquid extraction [6,23–30], and solid-phase extraction (SPE) [31,32]. We have earlier applied SPE for extraction of mono- and dicarboxylic acids, hydroxyacids, ketones, ketoacids, aldehydes, hydrocarbons, lactones and alcohols after aging of polyesters and degradable polyethylenes [4,7,8,16–18,33,34]. Identification and quantification of degradation products formed during hydrolysis of aliphatic polyesters can be a tedious procedure including many extraction steps. Extraction of all the desired hydrolysis products simultaneously in one step reduces both labor-time and loss of accuracy. The aim of this work was to develop a solid-phase extraction method for simultaneous extraction of dicarboxylic acids and diols from an aqueous media and with the developed SPE method and GC–MS, identify and quantify low-molecular-mass degradation products migrating from poly(butylene adipate) and poly(butylene succinate) during aging in water.

2. Experimental

2.1. Chemicals

Succinic acid (99%), glutaric acid (98%), adipic acid (99%), and 1,5-pentanediol (97%) used in SPE method development were all purchased from Fluka (Buchs, Switzerland) and used as received. 1,4-Butanediol (99%) was obtained from Riedel-de Haën (Seelze, Germany) and was also used as received. Water (HPLC grade) was purchased from Fluka while eluting solvents methanol (99.9%) and chloroform (99.5%) were purchased from Labscan (Dublin, Ireland) and acetonitrile (99.8%) from Merck Eurolab (Darmstadt, Germany). 1,4-Butanediol (BD) (99%), dimethyl ester of adipic acid (DMA) (∼99%) and dimethyl ester of succinic acid (DMS) (98%) used for synthesis of polyesters were purchased from Fluka (Buchs, Switzerland) and used as received. Titanium isopropoxide (TIP) (99.99%) used as catalyst, chloroform and diethyl ether used during synthesis were obtained from Sigma–Aldrich. Methanol used for precipitation of polyesters was obtained from Merck Eurolab.

2.2. Synthesis and hydrolysis of polyesters

PBS and PBA were synthesized by adding 1.05 mol BD and 1.0 mol DMS or DMA, respectively, to a two-neck round-bottom reaction vessel. 0.2 mol% of TIP catalyst was added to each reaction mixture. The reaction vessel was immersed in a silicon oil bath and the temperature was increased under nitrogen gas to 130 °C where the reaction was continued for 3 h. The methanol formed in the reaction was continuously distilled from the reaction mixture. The temperature of the reaction mixture was then raised to 180 °C under reduced pressure and the polymerization was continued for 16 h. After the polymerization was completed the reaction mixture was cooled down to room temperature and the PBA and PBS polymers were dissolved in chloroform and removed from the reaction vessel. The polymers were precipitated into methanol, filtrated and washed with diethyl ether. Number average molecular weight (relative to polystyrene standards) of PBA (10,500 g/mol) and PBS (9200 g/mol) was measured by size-exclusion chromatography (SEC) (Waters 717 plus auto sampler and a Waters model 510 SEC apparatus equipped with three Plgel 10 μm mixed-B columns, 300 mm × 7.5 mm and a PL-ELS 1000 detector). Chloroform was used as mobile phase at the velocity of 1 ml/min and polystyrene standards of 580, 1020, 2000, 5050, 9770, 19,800, 96,000, and 498,000 g/mol were used to calibrate the system.

An amount of 120 mg PBA and PBS were aged in 20 ml glass vials containing 10 ml water (HPLC grade from Fluka, Buchs, Switzerland). The vials were sealed by 5 M/l PTFE white-faced white silicone septas (20 mm diameter and 0.125 in. thick; 1 in. = 2.54 cm) from Supelco (Bellefonte, PA, USA). The sealed vials were aged in an oven at 37 °C (PBA and PBS) or 70 °C (PBS) for a period of 85 days. During this time vials were taken out continuously for analysis.

2.3. Development of SPE method

The expected final hydrolysis products of PBA and PBS are adipic acid, succinic acid, and 1,4-butanediol. Four different non-polar SPE sorbents were tested for their capability to simultaneously extract these compounds: Isolute C_8 (C_8 Octyl), Isolute C_{18} (C_{18} Octadecyl), Isolute C_{18}(EC) [C_{18} Octadecyl(end-capped)], and Isolute ENV+ (ENV+ hydroxylated polystyrene–divinylbenzene), all from Sorbent, Västra Frölunda, Sweden. C_8 and C_{18} are commonly used to extract organic compounds from aqueous matrixes. Their non-polar characteristics increase with increasing carbon chain length. End capping (EC) by trimethyl silane, reduces the number of silanol groups present at the surface and reduces the polar and ionic secondary interactions otherwise formed. ENV+ is especially

suited for extracting polar, and therefore very water soluble, analytes from aqueous matrixes. The solid phase is highly cross-linked and has higher capacity than normal C_{18} sorbents.

The solid phases were conditioned with 1 ml of methanol and equilibrated with 1 ml of water (pH < 2). pK_a of the analytes was 14.5 for 1,4-butanediol, 4.21 and 5.64 for the first and second hydroxyl group of succinic acid, and 4.41 and 5.41 for the first and second hydroxyl group of adipic acid. Controlling the pH of the sample is essential for performing an effective extraction. To avoid ionization of analytes when using non-polar interactions, pH of the sample was adjusted to a level that was at least two units lower than the pK_a of the analytes, i.e. pH < 2, by concentrated HCl. 3 ml of a solution containing known amount of adipic acid, succinic acid, 1,4-butanediol plus the internal standards, 1,5-pentanediol and glutaric acid, was applied to the SPE column. When the solution had passed through, the column was dried with a low flow of compressed air. To elute the analytes three different solvents were tested, i.e. methanol (0.1% HCl), acetonitrile, and chloroform, by applying 1 ml of eluting solvent to the solid phase. When acidic methanol (0.1% HCl) was used as an eluting solvent the dicarboxylic acids were methylized to methyl esters of respective acids. Due to losses of solvent in the solid phase, the samples were after elution diluted so that they all measured the volume of 1 ml. From the results of these tests, the solid-phase chosen for extraction of degradation products was ENV+ resin and eluting solvent methanol (0.1% HCl).

2.4. Extraction of degradation products

Identification and quantification of degradation products by gas chromatography–mass spectrometry, was preceded by extraction of produced substances trough the SPE procedure described in Section 2.3. The sample solution was separated from the polymer by filtration. Preliminary tests were done to estimate the concentration of the sample. If the estimated concentration was higher than 500 ng/μl, i.e. the upper concentration limit for linearity, the sample was diluted. One microliter of concentrated internal standard solution (1,5-pentanediol and glutaric acid, 3 g of internal standard/10 ml water) was added to the sample solution before the sample was applied to the SPE column. Quantification of degradation products was done through calibration curves and corrected with internal standards. Calibration curves were prepared by dissolving different amounts of adipic acid, succinic acid and 1,4-butanediol in water together with 1 μl of internal standard solution and extracting them with the SPE method described in Section 2.3. Concentrations for the analytes varied from 15 to 600 ng/μl.

2.5. Gas chromatography–mass spectrometry (GC–MS)

Identification and quantification of extracted degradation products was done by a ThermoFinnigan GCQ (San José, CA, USA.). The column used was a wall-coated open tubular (WCOT) fused silica CP-WAX 58 (FFAP)-CB column from Varian (25 m × 0.32 mm i.d., d_f 0.2 μm). Helium of scientific grade purity from AGA (Stockholm, Sweden) was used as carrier gas at the constant velocity of 40 cm/s (the electronic pressure control, EPC, of the GC was used to control the flow velocity). The initial oven temperature was 40 °C, which was held for 1 min. The oven was heated to 250 °C at the heating rate 10 °C/min, and held at 250 °C for 15 min. Electron impact mode, EI, was used with an electron energy of 70 eV. The mass-range scanned was 35–400 *m/z* and the ion source and transfer line temperatures were 180 and 250 °C, respectively. The injector temperature was set to 250 °C. One microliter of sample was injected in splitless injection mode and two blanks were run between each sample by injecting clean methanol (0.1% HCl). Identification of monomeric degradation products was confirmed by comparing their retention times and mass spectra to those of corresponding standard compounds. Oligomeric products were identified by their EI mass spectra and molecular ion produced obtained by running some of the samples in the CI mode with methane as a reagent gas.

2.6. Mass loss measurements

Mass loss measurements were conducted through weighting each filter, used to separate the polymer from the degradation media, before and after filtration on a Precisa 410AM-FR analytical balance. After filtration, the polymers were dried in desicator until constant weight, at which point the mass loss was calculated.

3. Results and discussion

3.1. Development of solid-phase extraction method

The expected final hydrolysis products from PBA and PBS, 1,4-butanediol, adipic acid and succinic acid, are all very water-soluble compounds. In addition 1,4-butanediol has a very high pK_a (14.5) while adipic acid and succinic acid have rather low pK_a values (4.41 and 5.41 for adipic acid and 4.21 and 5.64 for succinic acid), which make the simultaneous extraction from water even more difficult and rules out the use of ionic interactions. Four different non-polar SPE columns were tested to extract these compounds from water: C_8 silica, C_{18} silica, C_{18} silica (EC) and ENV+ resin. In addition to testing different solid-phases, three different eluting solvents were also tested: methanol (0.1% HCl), acetonitrile and chloroform. Chloroform and acetonitrile resulted in poor analyte elution repeatability and were therefore rejected as eluting solvents. Acidic methanol (0.1% HCl), however, resulted in repeatable elution of analytes and improved the GC behavior due to methylation of dicarboxylic acids to their methyl esters. To compare extraction efficiencies for the different sorbents tested, recoveries were

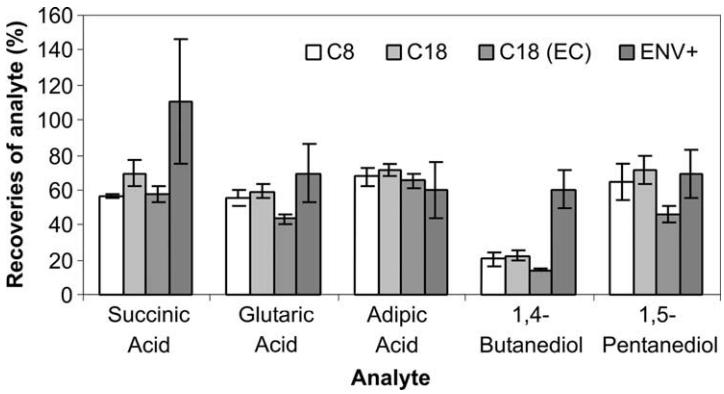

Fig. 1. Comparison of the different solid-phase extraction columns tested for the extraction of expected analytes and internal standards. Recoveries are calculated for a sample concentration of 300 ng/μl.

calculated for a sample concentration of 300 ng/μl, Fig. 1. Succinic acid was generally somewhat more difficult to extract than the slightly less polar adipic acid. ENV+ was the solid phase that resulted in the highest extraction efficiency for succinic acid and 1,4-butanediol, and that showed the smallest variations in extraction efficiency between the different analytes. This reduces diluting problems due to large difference in analyte concentrations.

Calibration curves ($r^2_{\text{adipic acid}} = 0.9511$, $r^2_{\text{succinic acid}} = 0.9597$, and $r^2_{\text{1,4-butanediol}} = 0.8835$) were made by dissolving known amounts of adipic acid, succinic acid and 1,4-butanediol in water and subjecting them to the earlier described SPE procedure. The linear ranges, 1–500 ng/μl for adipic acid and 2–500 ng/μl for 1,4-butanediol and succinic acid, were found by plotting the area of the analyte, divided by the area of respective internal standard, to the mass of the analyte. Different amounts of adipic acid, succinic acid and 1,4-butanediol were also dissolved in acidic methanol and analyzed by GC–MS. Extraction efficiencies were calculated by dividing the slope of the calibration curve made from extracted samples with the slope of a calibration curve made from non-extracted samples. Extraction efficiencies for the different analytes were 76% for 1,4-butanediol, 51% for succinic acid and 79% for adipic acid. Considering the different nature of the extracted compounds the recoveries obtained by this single step extraction were good. In comparison, Hirschlag and Köster have earlier developed a SPE method to extract different hydroxy acids and dicarboxylic acids from aqueous media [31]. They used a SDB-1 column from J.T. Baker and their recoveries for succinic and adipic acid were 84 and 67%, respectively. Relative standard deviations ($n = 6$), detection limits (S/N = 3) and quantification limits (S/N = 10) for the three analytes and internal standards are given in Table 1.

3.2. Identification and quantification of PBA and PBS hydrolysis products

The developed SPE method was applied to extraction of degradation products formed during hydrolysis of PBA and PBS. The extracted compounds were subsequently identified and quantified by GC–MS. Typical gas chromatograms with extracted degradation products are shown in Fig. 2. In addition to the monomeric products, dimers, i.e. hydroxybutyl adipate and hydroxybutyl succinate, and trimers, i.e. di(hydroxybutyl) adipate, di(hydroxybutyl) succinate and hydroxybutyl disuccinate were also detected. These compounds were identified by their molecular ion obtained with chemical ionization mode, CI, and analysis of their EI mode mass spectra. Identification of the oligomeric degradation products could not be confirmed by analysis of standard compounds but in the case of low temperature hydrolysis, the degradation products likely to be formed are the original monomers and dimers and trimers which further supports the identification. The amount of monomeric hydrolysis products formed after different hydrolysis times is given

Table 1
Detection limits (S/N = 3), quantification limits (S/N = 10) and relative standard deviations (R.S.D.) for the expected analytes

Analyte	S/N = 3, concentration (ng/μl)	S/N = 10, concentration (ng/μl)	R.S.D. (%)[a]
Succinic acid, dimethyl ester	2	7	7
Glutaric acid, dimethyl ester	1	2	
Adipic acid, dimethyl ester	1	3	4
1,4-Butanediol	2	6	3
1,5-Pentanediol	2	7	

[a] R.S.D. values for extracted degradation products, corrected with respective internal standard, were calculated from six extractions made the same day.

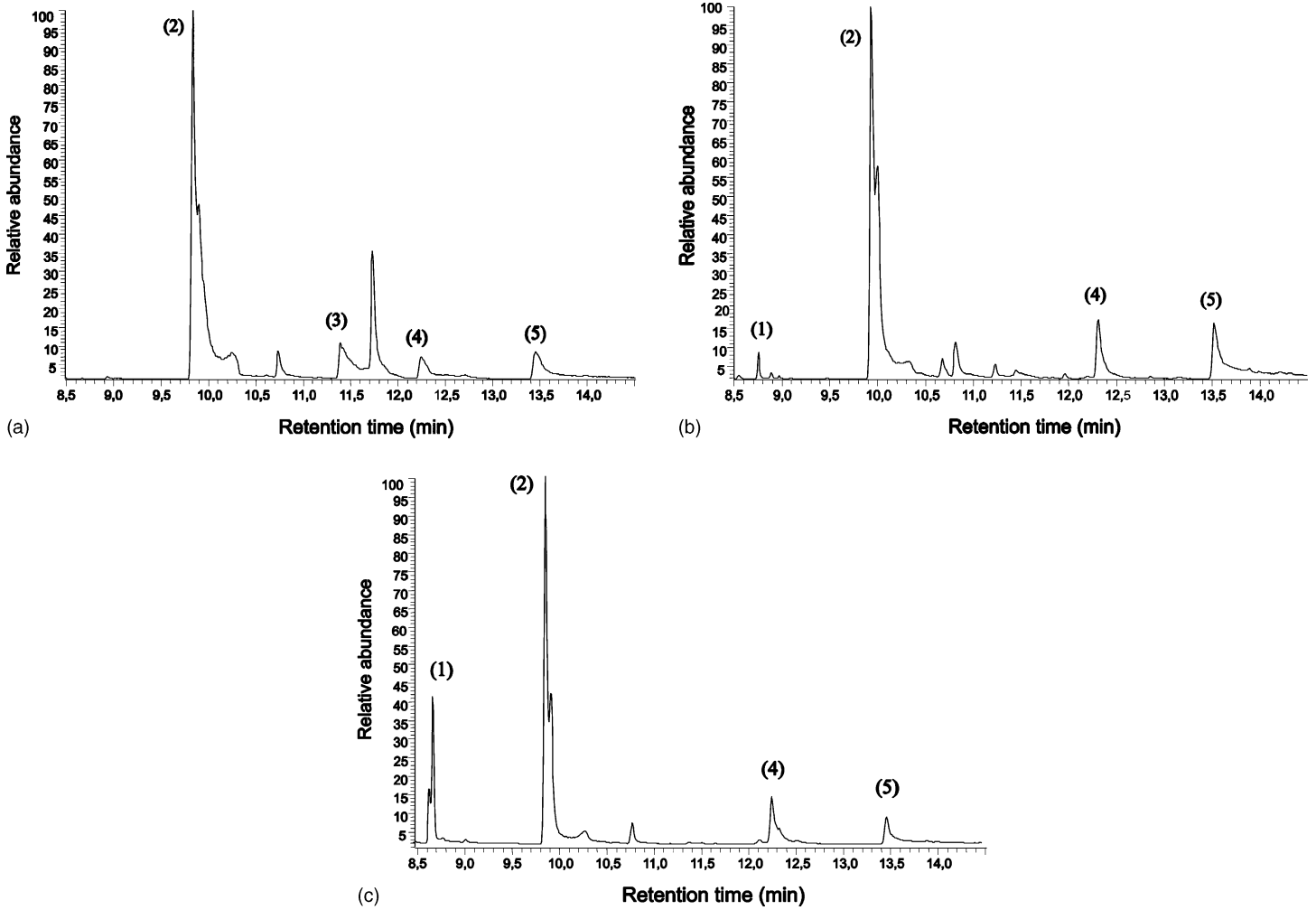

Fig. 2. Gas chromatograms showing the hydrolysis products extracted from (a) poly(butylene adipate) after 3 weeks at 37 °C; (b) poly(butylene succinate) after 3 weeks at 37 °C; (c) poly(butylene succinate) after 3 weeks at 70 °C. The identity of the numbered peaks is (1) succinic acid, dimethyl ester, (2) glutaric acid, dimethyl ester (internal standard), (3) adipic acid, dimethyl ester, (4) 1,4-butanediol, (5) 1,5-pentanediol (internal standard).

Table 2
The amount of succinic acid, adipic acid, and 1,4-butanediol formed during hydrolysis of poly(butylene adipate) in water at 37 °C and poly(butylene succinate) in water at 37 or 70 °C

Days	Adipic acid formed at 37 °C[a]	1,4-Butanediol formed at 37 °C[a]	Succinic acid formed at 37 °C[b]	1,4-Butanediol formed at 37 °C[b]	Succinic acid formed at 70 °C[b]	1,4-Butanediol formed at 70 °C[b]
0	<QL[c]	1.0 ± 0.3	<DL[d]	3.1 ± 0.4	<DL[d]	3.1 ± 0.4
7	6.5 ± 3.3	8.9 ± 2.6	<QL[c]	16 ± 5.4	23 ± 13	32 ± 4.5
22	8.2 ± 2.6	22 ± 1.5	4.2 ± 0.6	36 ± 1.5	42 ± 1.0	58 ± 5.5
57	21 ± 0.7	22 ± 0.8	21 ± 0.9	53 ± 6.5	730 ± 5.8	430 ± 20
85	28 ± 0.1	23	21 ± 0.6	39 ± 3.4	1400 ± 55	750 ± 26

[a] Amounts are given in mg/mg PBA ($\times 10^{-4}$).
[b] Amounts are given in mg/mg PBS ($\times 10^{-4}$).
[c] Amounts QL: quantification limit (S/N = 10).
[d] Amounts DL: detection limit (S/N = 3).

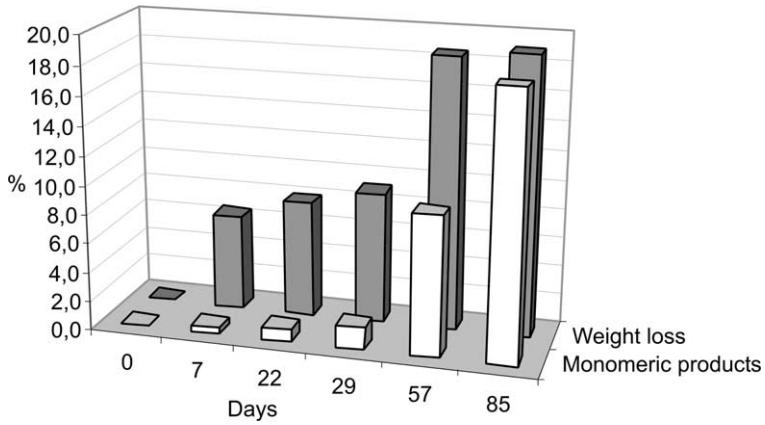

Fig. 3. Comparison of observed weight loss (%) and the amount of monomeric degradation products from PBS after different hydrolysis times in water at 70 °C. The amount of monomeric degradation products is given as % of the theoretical amount if the polymer was totally hydrolyzed to monomers.

in Table 2. Similar amounts of hydrolysis products were formed from the two polyesters, PBA and PBS, during aging at 37 °C. However, large increase in the hydrolysis rate and the amount of water-soluble hydrolysis products was detected when the aging temperature was raised to 70 °C.

3.3. Correlation between detected low-molecular-mass products and mass loss

Paralleled to the analysis of degradation products, mass loss for the hydrolyzed polyesters was measured after different aging times. PBA and PBS were rather stable towards low temperature hydrolysis and only 6–7% weight loss was observed after 85 days at 37 °C. Similar mass loss was observed after only 7 days when PBS was aged at 70 °C. The mass loss observed for PBA and PBS after different hydrolysis times at 37 °C was significantly larger than the amount of monomeric products formed. This shows that the initial weight loss is mainly due to the release of water-soluble oligomers, a conclusion consistent with earlier results obtained for other polyesters [7]. As seen in Fig. 3, similar behavior was initially observed during aging at 70 °C, i.e. the mass loss was larger than the amount of monomeric hydrolysis products. However, on prolonged aging the water-soluble oligomers were further hydrolyzed to monomers and after 85 days of aging at 70 °C, the total amount of monomeric degradation products formed from PBS approximately equals the mass loss. A more detailed study of the hydrolysis will be reported in a later paper.

4. Conclusion

A rapid solid-phase extraction method was developed to simultaneously extract dicarboxylic acids and diols formed during hydrolysis of poly(butylene succinate) and poly(butylene adipate). Four different non-polar SPE columns were tested for the extraction of adipic acid, succinic acid and 1,4-butanediol, the final hydrolysis products of PBA and PBS. ENV+ resin, a polystyrene based sorbent showed the best extraction efficiency for 1,4-butanediol and succinic acid, as well as least variation in extraction efficiency between the expected analytes. Good repeatability and low detection limits enabled quantification of degradation products at early stages of hydrolysis. The identified hydrolysis products included the monomers, succinic acid, adipic acid and 1,4-butanediol and several dimers and trimers. The observed weight loss was generally

considerably higher than the amount of monomeric hydrolysis products showing that mainly oligomeric degradation products are released from the materials. After prolonged aging at elevated temperature, i.e. after 85 days at 70 °C, the oligomeric products were almost totally further hydrolyzed to monomers. The combination of GC–MS and an effective extraction method is a powerful tool to obtain information on degradation rates, mechanisms, and product formation during hydrolysis of polyesters.

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