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Qualitative and quantitative solid-phase microextraction gas chromatographic–mass spectrometric determination of the low-molecular-mass compounds released from poly(vinyl chloride)/polycaprolactone–polycarbonate during ageing

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Abstract

A solid-phase microextraction (SPME) method was developed to quantitatively determine the amount of 6-hydroxyhexanoic acid in aqueous solutions. The SPME method in combination with GC–MS was then applied to identify and quantify the low-molecular-mass compounds migrating from a new poly(vinyl chloride) (PVC) material, PVC/polycaprolactone–polycarbonate (PCL–PC) during ageing in water. It was shown that only a small amount of 6-hydroxyhexanoic acid, the final hydrolysis product of PCL–PC, migrated from the blend during ageing at 37 and 70 °C. If, however, the temperature was raised to 100 °C rapid hydrolysis of PCL–PC resulted. In addition to 6-hydroxyhexanoic acid, 6-hydroxyhexanoic acid dimer, caprolactone, different carboxylic acids, acetophenone and phenol were identified. SPME–GC–MS was also applied to monitor the low-molecular-mass compounds migrating from the PVC/PCL–PC blend during thermo-oxidation.

Keywords: Solid-phase microextraction; Poly(vinyl chloride); Polyester–polycarbonate; 6-Hydroxyhexanoic acid

1. Introduction

The environmental impact of polymeric materials is largely determined by the low-molecular-mass compounds released from the material. Qualitative and quantitative determination of these compounds is especially important in the safety assessment of plastic materials to be used in for example medical applications, children's toys and food packaging. Gas chromatography–mass spectrometry (GC–MS) in combination with appropriate extraction method is a perfect tool to identify and quantify volatile or semi-volatile organic compounds including different low-molecular-mass compounds in polymeric materials [1–3]. Solid-phase microextraction (SPME) is a relatively new, inexpensive, rapid and solvent-free extraction technique [4]. It is based on a typically, 1-cm-long, thin fused-silica fibre coated with a polymeric stationary phase. For sampling the fibre is immersed directly into aqueous samples or in the headspace over the liquid or solid sample matrix. During extraction the analytes are adsorbed or absorbed by the fibre, depending on the type of

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stationary phase used [5]. After completed extraction the SPME fibre is placed in the injection port of a GC system where the analytes are thermally desorbed and transferred to the capillary column. Several external factors like temperature, pH, salting and agitation influence the extraction efficiency, while the fibre material affects the selectivity of the extraction.

Since its introduction in the 1990s SPME has rapidly found numerous applications in environmental, food, pharmaceutical, clinical and forensic applications [6]. There are still only a few publications where SPME has been used for extraction of low-molecular-mass compounds from polymeric materials. However, we have in several studies shown the applicability of SPME in extracting different low-molecular-mass compounds from polymeric materials including degradation products [7–9] and additives [10]. SPME has also been applied to extraction of odour compounds [11] and monomers [12] from polymeric materials and to extraction of polymer additives from food simulants [13] or water samples [14].

Plasticised poly(vinyl chloride) (PVC) is used in children's toys and in several medical applications including blood bags and different tubings. Plasticised PVC has many favourable properties, but the migration of low-molecular-mass plasticisers from PVC products when in contact with different body fluids or other aqueous environments is a point of concern [15,16]. This is especially serious since some of the most common PVC plasticisers are suspected for serious health effects [17–19]. Several authors have studied the migration of low-molecular-mass plasticisers, such as di(2-ethylhexyl)adipate [20–22] or di(2-ethylhexyl)phthalate (DEHP) [23,24] into food or food simulants. The migration of different phthalates from PVC toys and childcare articles into saliva and saliva simulant has also been investigated [25,26]. The long-term fate of PVC products and their additives in landfills was recently reviewed by Mersiowsky [27].

A promising and appealing way to obtain safe plasticised PVC grades is to substitute phthalates with compatible and non-toxic polymeric plasticisers. A polymeric plasticiser compatible with PVC is, due to its molecular dimensions less likely to migrate from the PVC product. The literature reports PVC blends with different rubber-like materials, e.g., acrylonitrile–butadiene rubber or vinylchloride–ethylene–vinylacetate [28,29] or with aliphatic polyesters including polycaprolactone [30,31], poly(3-hydroxybutyrate–co-3-hydroxyvalerate) [32] and poly(butylene adipate) [33]. Generally in these studies the compatibility and other material properties were studied, while long-term properties or possible migration of the new plasticisers were not investigated. There are, however, a few studies where the migration poly(butylene adipate) from PVC films to food was investigated [34–36].

To ensure the safety of the new PVC materials in, e.g., medical applications, the release rate of the new plasticisers and their degradation products have to be determined. The aim of the present work was to develop a SPME method for qualitative and quantitative determination of the low-molecular-mass compounds migrating from a new PVC material, plasticised with polycaprolactone–polycarbonate (PCL–PC), during ageing in aqueous environments. The method should reproducibly extract the hydrolysis products of the new plasticiser, PCL–PC, and also be able to extract other low-molecular-mass compounds, e.g., additives and additive degradation products that may migrate from the blend during ageing.

2. Experimental

2.1. Materials

The PCL–PC was synthesised by Professor Ferruti at the University of Milan in Italy and by Polymer Labs. (Church Stretton, UK). The number average molecular mass (M_n) for the synthesised PCL–PC was 32 700 and the weight average molecular mass (M_w) was 52 500 as determined by size-exclusion chromatography (SEC) at Polymer Laboratories. PVC was a commercial medical grade PVC K70M. Tubes made of PVC/PCL–PC were extruded at EVC Compounds (Argenta, Italy). The blend composition was 100 parts of PVC and 58 parts of PCL–PC. The blend also contained epoxidised soya bean oil and a mixture of commercial stabilisers. The synthesis of PCL–PC, as well as its use as a

plasticiser for PVC has been patented by EVC Compounds [37,38].

2.2. Degradation procedure

PVC/PCL–PC blends were aged in 20-ml headspace vials (from Chrompack, Middelburg, The Netherlands). The vials were closed with PTFE-silicone-rubber septum cap from Perkin-Elmer (Stockholm, Sweden). For ageing in aqueous environment 1 g of the PVC/PCL–PC blend was closed in each vial together with 5 ml water (HPLC grade from Fluka, Buchs, Switzerland). The vials were placed in a conventional circulating air oven (Heraeus, Hanau, Germany) and aged at 37, 70 or 100 °C. The ageing time varied from 1 to 98 days for the samples aged at 37 or 70 °C and from 1 to 70 days for the samples aged at 100 °C. Samples were also aged at elevated temperature in air. For these thermo-oxidation studies 0.5 g of PVC/PCL–PC blend was put in each vial and aged for 7 days at 100 °C. After each ageing time and temperature three vials were taken out for analysis.

2.3. SPME of aqueous samples

A 2-ml volume of water (sample solution) was taken from each vial after oven ageing and the low-molecular-mass products that had migrated from the blend were extracted by SPME. A 10-μl volume of internal standard solution containing 10 μl pentanoic acid/ml water was added to each sample solution before the extraction. The area for the pentanoic acid peak was then used to correct for the possible errors during extraction or injection. The SPME fibre chosen for the extraction was a 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) fibre (from Supelco, Bellefonte, PA, USA). The fibre was immersed into the aqueous phase for 30 min to extract the low-molecular-mass products from water or buffer. The aqueous phase was agitated at constant velocity during the extraction and a sampling stand was used to position the fibre in the sample consistently. The SPMEs were then analysed by GC–MS. Mass spectra was used to identify the unknown compounds and their identity was confirmed by running corresponding standard compounds. The identification was positive if the retention time and mass spectra of the standard compound were identical with those of the unknown compound.

Nine different concentrations of standard 6-hydroxyhexanoic acid ranging from 1 to 1000 μg/ml together with known amount of internal standard solution were dissolved in water (HPLC grade from Fluka) and phosphate buffer (1.0 *M*, pH 7.4 from Sigma–Aldrich, Sweden). These standard solutions were then extracted with the same SPME method and analysed with GC–MS. For comparison calibration curves were prepared with both external and internal calibration. Due to the high concentration of 6-hydroxyhexanoic acid in the samples aged between 21 and 70 days at 100 °C only 1 ml of sample solution was taken from these samples. This 1 ml was diluted with water to 2 ml and extracted as the other samples. The amount of 6-hydroxyhexanoic acid obtained from the calibration curve was then multiplied by 2. From the calibration curve we obtained the concentration of 6-hydroxyhexanoic acid/ml water. To obtain the total amount released from 1 g of PVC/PCL–PC blend, this amount was multiplied by 5 (1 g of PVC/PCL–PC was aged in 5 ml water).

2.4. Headspace SPME of thermo-oxidised samples

The low-molecular-mass products formed during thermo-oxidation were extracted with SPME from the headspace above the PVC/PCL–PC blend. The SPME fibre was the same 65 μm PDMS–DVB fibre (Supelco) that was used for the extractions from water. The extraction time was 30 min and the extraction temperature was 70 °C.

2.5. Gas chromatography–mass spectrometry

The GC–MS analyses were performed on a ThermoFinnigan GCQ instrument (San José, CA, USA). The column used was a wall-coated open tubular (WCOT) fused-silica CP WAX 58 capillary column (25 m×0.32 mm I.D., film thickness 0.25 μm) from Varian. The column temperature was initially held at 40 °C for 1 min. The temperature was then increased to 250 °C at a heating rate of 10 °C/min and then held at 250 °C for 10 min. Helium (99.9999%, from AGA, Stockholm, Sweden) was used as carrier gas

with a constant velocity of 40 cm/s. The extracted degradation products were desorbed from the SPME fibre by placing the fibre in the injector of the GC system for 5 min at 225 °C. The injector was operated in the splitless mode. To identify and quantify the products MS was run in the electron impact (EI) mode with an electron energy of 70 eV. The detector was scanned in the mass-range from 35 to 400 m/z with a scan time of 0.43 s. The temperatures of the ion source and the transfer line were 180 and 275 °C, respectively.

3. Results and discussion

3.1. Analysis of the low-molecular-mass compounds released from PVC/PCL–PC

The low-molecular-mass compounds migrating from the new PVC/PCL–PC material during ageing in aqueous environment and during thermo-oxidation were extracted and identified by SPME–GC–MS. At the same time quantitative analysis of 6-hydroxyhexanoic acid the final hydrolysis product of PCL–PC was performed. The compounds extracted from water after ageing at 37 and 70 °C included 6-hydroxyhexanoic acid, different carboxylic acids probably originating from epoxidised soya bean oil and some other, e.g., synthesis related compounds. When the ageing temperature was raised to 100 °C dimer of 6-hydroxyhexanoic acid and caprolactone were also identified. As seen from Fig. 1 carboxylic acids dominated the chromatograms during ageing at 37 °C, but when the ageing temperature was raised to 100 °C 6-hydroxyhexanoic acid became the most abundant low-molecular-mass compound.

The chromatogram in Fig. 2 shows the compounds that migrated from PVC/PCL–PC during thermo-oxidation at 100 °C. The identified compounds included caprolactone and 6-hydroxyhexanoic acid. The different carboxylic acids and 6-hydroxyhexanoic acid dimer that migrated from the material during ageing in water were not detected. Since we have in earlier studies used headspace SPME to extract decanoic acid and dodecanoic acid from thermo-oxidised polyethylene [7], these compounds are known to be volatile enough to be extracted by headspace SPME indicating that the carboxylic acids did not migrate from the material during ageing in air. The compounds identified after ageing in aqueous environments and after thermo-oxidation are compared in Table 1.

3.2. Quantitative determination of 6-hydroxyhexanoic acid

Fig. 3 shows the amount of 6-hydroxyhexanoic acid that migrated from 1 g of PVC blend as a function of ageing time at different temperatures. As seen in Fig. 3a already after 1 day at 37 °C trace amounts of 6-hydroxyhexanoic acid were detected. This 6-hydroxyhexanoic acid is probably present in the virgin material since 1 day at 37 °C is too short a time to hydrolyse PCL–PC, especially when it is partly protected by PVC. This is supported by the almost constant amount of 6-hydroxyhexanoic acid detected during ageing at 37 °C. At 70 °C the amount of 6-hydroxyhexanoic acid formed from 1 g of PVC/PCL–PC blend, containing approximately 350 mg PCL–PC, increased from 0.01 mg after 1 day to 0.15 mg after 98 days. This means that even when temperature was raised to 70 °C less than 0,04% of the PCL–PC polymer degraded to 6-hydroxyhexanoic acid during 98 days. Fig. 3b shows the large increase in the hydrolysis rate and the amount of 6-hydroxyhexanoic acid that migrated from the blend, when aging temperature was raised to 100 °C. In addition to 6-hydroxyhexanoic acid, 6-hydroxyhexanoic acid dimer and caprolactone were detected and identified as PCL–PC degradation products. Non water-soluble oily compounds, assumed to be longer PCL–PC oligomers, were also seen on the walls of the vials. In accordance with these results the mass losses were only 0.2 and 0.8% after 98 days at 37 and 70 °C, respectively, while the mass loss after 70 days at 100 °C was over 30%.

The amount of different carboxylic acids was not quantified, but a few standard solutions with different amounts of carboxylic acids were analysed and the amount of decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid and octadecanoic acid that migrated from 1 g of PVC blend during ageing at 37 °C was estimated to be between 2 and 6 μg/acid. The amount of shorter carboxylic acids remained fairly constant after 7 days, while the

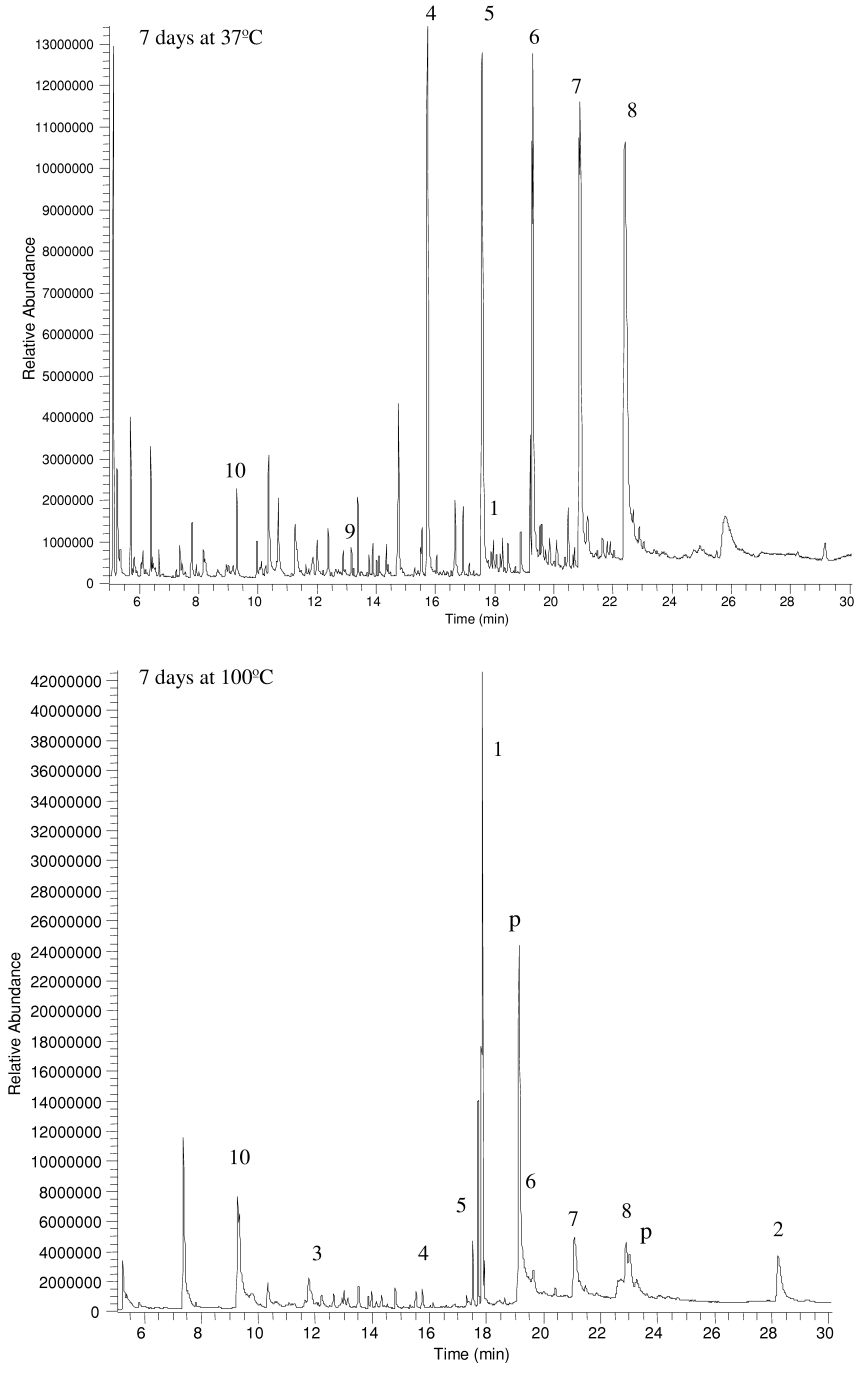

Fig. 1. GC–MS chromatograms showing the low-molecular-mass compounds extracted from sample water after 7 days at 37 and 100 °C. Peaks: 1=6-hydroxyhexanoic acid, 2=6-hydroxyhexanoic acid dimer, 3=caprolactone, 4=decanoic acid, 5=dodecanoic acid, 6=tetradecanoic acid, 7=hexadecanoic acid, 8=octadecanoic acid, 9=phenol, 10=acetophenone, p=phthalate.

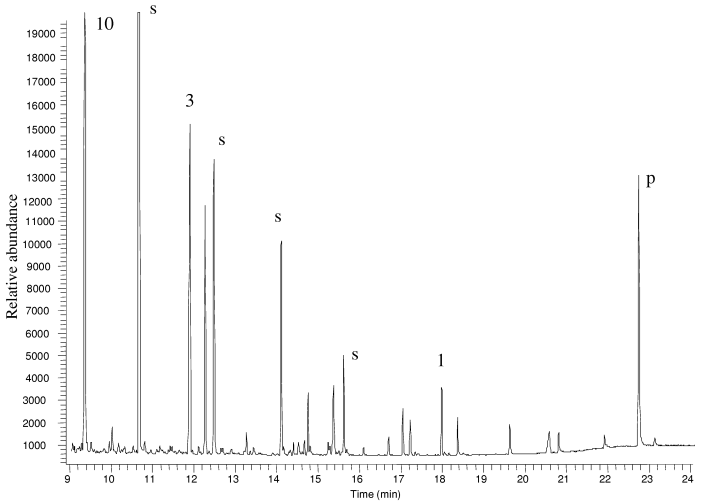

Fig. 2. GC–MS chromatogram after 7 days of thermo-oxidation at 100 °C. Peaks: 1=6-hydroxyhexanoic acid, 3=caprolactone, 9=phenol, 10=acetophenone, p=phthalate, s=system peak.

amount of hexadecanoic and octadecanoic acid increased until 40 days and then remained constant.

3.3. The developed solid-phase microextraction method

To quantify the amount of 6-hydroxyhexanoic acid that migrate from PVC samples different amounts of standard 6-hydroxyhexanoic acid together with constant amount of internal standard were dissolved in water, extracted by SPME and analysed by GC–MS. Some hydroxyacids, e.g., 2-hydroxyhexanoic acid and 2-hydroxyisobutyric acid, were first tested as internal standards. However, probably due to the

Table 1
Comparison of the low-molecular-mass compounds released from PVC/PCL–PC during aging in aqueous environments and during thermo-oxidation

t_R (min)	Compound	Water, 37 °C	Water, 70 °C	Water, 100 °C	Air, 100 °C
17.8	6-Hydroxyhexanoic acid[a]	x	x	x	x
28.1	6-Hydroxyhexanoic acid dimer[a]			x	
11.7	Caprolactone[a]			x	x
14.7	Nonanoic acid[b]	x	x	x	
15.7	Decanoic acid[b]	x	x	x	
16.7	Undecanoic acid[b]	x	x	x	
17.5	Dodecanoic acid[b]	x	x	x	
18.4	Tridecanoic acid[b]	x	x	x	
19.2	Tetradecanoic acid[b]	x	x	x	
20.1	Pentadecanoic acid[b]	x	x	x	
20.9	Hexadecanoic acid[b]	x	x	x	
21.6	Heptadecanoic acid[b]	x	x	x	
22.4	Octadecanoic acid[b]	x	x	x	
9.2	Acetophenone	x	x	x	x
13.1	Phenol[c]	x	x	x	x

[a] Degradation product of PCL–PC.
[b] Epoxidised soya bean oil.
[c] Synthesis related compound.

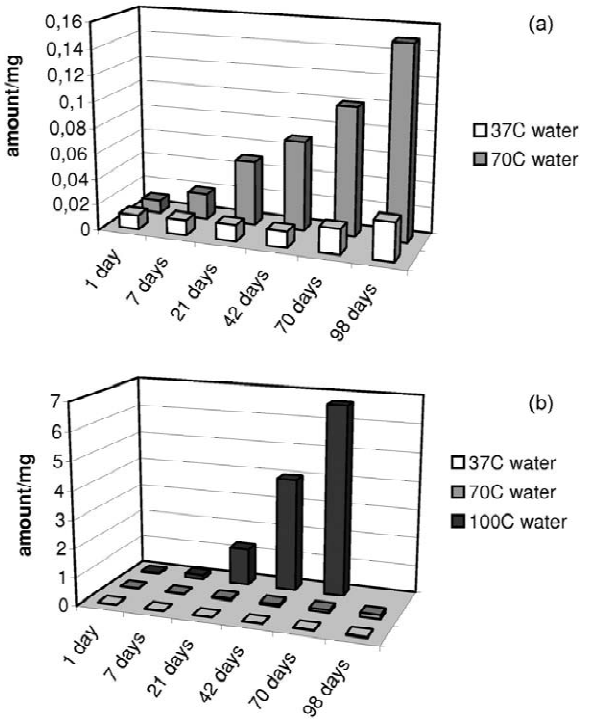

Fig. 3. The amount of 6-hydroxyhexanoic acid released from PVC/PCL–PC during aging in water at (a) 37 and 70 °C and (b) 37, 70 and 100 °C.

different position of the hydroxy group, the relative responses obtained with subsequent GC–MS analysis were much lower than for 6-hydroxyhexanoic acid. Pentanoic acid was chosen as an internal standard because it, due to its carboxylic acid group, should be affected by, e.g., pH changes in a similar way than 6-hydroxyhexanoic acid. It also did not co-elute with any of the analytes in the PVC samples. For comparison nine-point calibration curves were prepared using both internal and external calibration. Both curves exhibited linear behaviour over the studied rather wide concentration range (1–1000 μg/ml). The correlation coefficients for linearity were $r^2=0.988$ for external calibration and $r^2=0.980$ for internal calibration. To test the effect of different sample matrixes different concentrations of 6-hydroxyhexanoic acid were also extracted from phosphate buffer (pH 7.4). The correlation coefficients were slightly lower compared to those obtained for water extractions e.g., $r^2=0.974$ and $r^2=0.982$ for external and internal calibration, respectively. The relative responses from GC–MS analysis were around 10 times lower compared to the responses obtained when the same amount of 6-hydroxyhexanoic acid was extracted from water. This is probably due to the larger amount of dissociated acid groups in phosphate buffer, which makes the extraction less effective.

The extraction efficiency of the polar 6-hydroxyhexanoic acid by the PDMS–DVB fibre was rather low. As a comparison the relative responses for the extracted carboxylic acids (C_{10}, C_{12}, C_{14}, C_{16} and C_{18}) were around two orders of magnitude larger than those obtained for corresponding amount 6-hydroxyhexanoic acid. The detection limit was estimated to be 1 μg/ml from extracted ion chromatograms at a 10:1 S/N ratio. This sensitivity was, however, considered adequate since the lowest amounts in the PVC samples to be analysed were around 2 μg/ml. The relative standard deviation ($n=6$) for the extraction of 6-hydroxyhexanoic acid was 8%.

In addition to 6-hydroxyhexanoic acid, several carboxylic acids migrated from the PVC/PCL–PC blends during ageing. The total concentration of these carboxylic acids was, however, rather low and it did not significantly affect the pH the sample solution. To test the influence of carboxylic acids on the extraction of 6-hydroxyhexanoic acid, standard solutions with known amounts of 6-hydroxyhexanoic acid together with different carboxylic acids were prepared, extracted by SPME and analysed with GC–MS. The comparison of the responses obtained for extractions with and without carboxylic acids showed that the extraction efficiency for 6-hydroxyhexanoic acid was not affected by low concentrations of carboxylic acids. Larger concentration of carboxylic acids could, however, significantly lower the pH of the sample solution and would probably affect the extraction efficiency for 6-hydroxyhexanoic acid.

4. Conclusions

SPME was shown to be a rapid sample preparation technique for quantitative determination of 6-hydroxyhexanoic acid migrating from a new PVC/PCL–PC material during aging in water. Reproducible results were obtained and standard deviations

were in the range usually obtained for similar SPMEs. Only small amounts of 6-hydroxyhexanoic acid migrated from the blend during ageing at 37 and 70 °C, while a large increase in the hydrolysis rate and the amount of 6-hydroxyhexanoic acid migrating from the blend was observed when the ageing temperature was raised to 100 °C. SPME–GC–MS also provided qualitative information of the other low-molecular-mass products migrating from PVC/PCL–PC blend during ageing in aqueous environment and during thermo-oxidation. The identified low-molecular-mass compounds included degradation products of PCL–PC, i.e., 6-hydroxyhexanoic acid, dimer of 6-hydroxyhexanoic acid and caprolactone, several carboxylic acids probably originating from the epoxidised soya bean oil and other, e.g., synthesis related compounds (phenol, acetophenone).

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