Assessment of the degradation of polyurethane foams after artificial and natural ageing by using pyrolysis-gas chromatography/mass spectrometry and headspace-solid phase microextraction-gas chromatography/mass spectrometry

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ABSTRACT

Polyurethane foams are widely present in museum collections either as part of the artefacts, or as a material for their conservation. Unfortunately many of PU foam artefacts are in poor condition and often exhibit specific conservation issues. Their fast thermal and photochemical degradations have been the aim of previous researches. It is now accepted that hydrolysis predominates for polyester-based polyurethane PU(ES) whereas oxidation is the principal cause of degradation for polyether-based polyurethane PU(ET) variety. Only a few studies have been devoted to volatile organic compounds (VOCs) emitted by polyurethanes and, to our knowledge, none were performed on polyurethane foams by using headspace-solid phase microextraction (HS-SPME). The objective of the work described here is to assess the impact of some environmental factors (humidity, temperature and daylight) on the degradation of PU foams by evaluating their volatile fractions. We investigated morphological changes, polymerized fractions and volatile fractions of (i) one modern produced PU(ES) foam and one modern PU(ET) foam artificially aged in different conditions as well as (ii) four naturally aged foams collected from various daily life objects and selected for the representativeness of their analytical data. Characterization procedure used was based on attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and non-invasive headspace solid-phase microextraction coupled with gas chromatography and mass spectrometry (HS-SPME-GC/MS). In this paper, the formation of alcohol and acid raw products for PU(ES) and glycol derivatives for PU(ET) during natural and artificial ageing is confirmed. These main products can be considered as degradation markers for PU foams. Results show that artificial and natural ageing provide similar analytical results, and confirm that the dominant degradation paths for PU(ES) and for PU(ET) are hydrolysis and photo-oxidation, respectively. Lastly, we highlight that non-invasive HS-SPME-GC/MS analysis allows to distinguish between PU(ES) and PU(ET) at any point of their degradations.

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1. Introduction

Polyurethane (PU) is a large family of polymers whose composition has evolved over time. Polyurethane foams are widely present in museum collections such as natural history museums, fine art museums, modern art museums, either as part of the artefacts, or as a material for their conservation (stuffing, protection, packing and storage) [1–15]. Among museum collections they feature predominantly as sculptures, design objects, cushioning materials, textiles, and toys. Polyurethane foams are also largely used in home furniture, automobiles, and thermal insulation [16–18]. Unfortunately many of PU foam artefacts are in poor condition and often exhibit specific conservation issues. Polyurethane foams

particular instability has been previously recognized [19,20]. The resistance of polyurethane to ageing is mainly dependent on the composition of the raw materials used during their manufacture. It has been previously reported that the main degradation paths for polyurethane foams are a combination of hydrolysis, thermal oxidation and/or photo-oxidation. It is now accepted that hydrolysis predominates for polyester-based polyurethane PU(ES) whereas oxidation is the principal cause of degradation for polyether-based polyurethane PU(ET) variety [12,16–18]. PU foams degrade more rapidly than other forms of polyurethanes because they are very porous, and this porosity makes the polymer accessible to environmental oxygen, light and moisture. This fast thermal and photochemical ageing has been the aim of many researches [21–24]. Analytical methods most commonly used previously for studying polyurethane degradations are: infrared spectroscopy (IR) [1,4,6,9,12,25–28], gas chromatography coupled with mass spectrometry (GC/MS) [29–35], thermogravimetry (TG), differential

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scanning calorimetry (DSC) [36–39] and size-exclusion chromatography (SEC) [40,41]. During ageing, low molecular weight compounds, either degraded or residual products from manufacturing are emitted from the polyurethane matrix. Only a few studies have been devoted to volatile organic compounds (VOCs) emitted by polyurethanes [42–44] and, to our knowledge, none were performed on polyurethane foam by using headspace-solid phase microextraction (HS-SPME). Nevertheless, first reported by Pawliszyn and co-workers [45–47], SPME is a sensitive, reliable and fast method which is extensively used for trapping and removing volatile organic compounds. In recent years, its use has been extended to the analysis of a wide variety of matrices and a large range of analytes [48] among which are synthetic polymers [42–44,49–53]. Moreover, SPME can be envisioned as a non-invasive analytical method well suited for museum artefacts. This method has thus gained widespread acceptance in the field of cultural heritage and has been already successfully applied for the characterisation of various museum objects [54–59].

The aim of this study is to assess the impact of humidity, temperature and daylight on the degradation of PU foams by evaluating the volatile fraction. We investigated morphological changes, polymerized fractions and volatile fractions of (i) one modern produced PU(ES) foam and one modern PU(ET) foam artificially aged in different conditions as well as (ii) numerous naturally aged foams collected from various daily life objects kept at room temperature. Among naturally aged foams studied, we are presenting four foams because of the representativeness of their analytical data. The characterization methods were based on visual observations (binocular), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and headspace-solid phase microextraction coupled with gas chromatography and mass spectrometry (HS-SPME-GC/MS). In addition, naturally aged foams were preliminary characterized using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). Infrared data were also collected from modern foams after artificial ageing.

From all artificially and naturally aged samples, the visual observations and Py-GC/MS data agreed with the literature [1,12,16–18]. It showed that polyester-based polyurethanes are more sensitive to thermal ageing in humid conditions, by hydrolysis, and less sensitive to light ageing. Conversely, polyether-based polyurethanes degrade primarily by photo-oxidation and have higher resistance to hydrolysis. PU(ES) foam did not exhibit changes induced by thermal dry ageing or light ageing and PU(ET) was not affected by thermal (humid and dry) ageing.

In this paper, after the brief presentation of the infrared spectroscopy-based identifications of the four selected naturally aged samples, we discuss the main morphological changes and Py-GC/MS data obtained from the more affected modern foams, i.e. the PU(ES) aged in thermal humid condition and the PU(ET) foam aged photochemically. These analytical data are compared with those obtained from the naturally aged foams. It provides PU foam fingerprints highlighting potential chemical markers that inform us about the mechanisms and the degradation rate of PU foams. A particular attention was also devoted to volatiles emitted by the same set of samples. We showed the ability of SPME tool for trapping VOCs emitted by PU(ES) and PU(ET) foams at any point of their degradations allowing further identification by GC/MS. Compositions of the volatile fractions upon artificial ageing were compared with those obtained from the naturally aged foams, and the relevance of artificial ageing applied to simulate natural degradation has also been commented.

The present research was carried out in the frame of the European project POPART: strategy for the preservation of plastic artefacts in museum collections.

2. Experimental

2.1. Modern foams study

Two different types of modern PU foams, supplied by Raja France, were first selected as reference for producing samples from either ether or ester based foams type. The ether foam is grey foam in which the isocyanate hard domain is made up of aromatic toluene diisocyanate (TDI). TDI consists of a mixture of the 2,4- and 2,6-diisocyanatetoluene isomers and the polyol soft domain is based on polypropylene glycol (PPG). The ester foam is red foam in which the isocyanate hard part is also made up of a mixture of the 2,4- and 2,6-TDI and the polyol soft part is based on adipate ester. Ether and ester foams are both flexible foams with a density of $22 \, kg/m^3$ and $25 \, kg/m^3$, respectively. Foam additives, blowing agent and dyes added were unknown.

2.2. Artificial ageing

These two types of modern foams were subjected to thermal ageing in dry and humid conditions and to light ageing. Before ageing, they were cut into small squares ($5 \, cm \times 5 \, cm$) and placed on glass plates. Ageing were performed in open space.

2.2.1. Thermal (dry and humid) ageing

Samples were placed into Heraeus Vötsch HC 0020 controlled ovens ($90 \pm 2 \, °C$ and relative humidity below 10% for dry condition; $90 \pm 2 \, °C$ and 50% relative humidity for humid condition). They were aged up to 40 weeks and aged samples were removed from the oven every week for humid ageing and every two weeks for dry ageing.

2.2.2. Light ageing

Samples were placed into a Servathin controlled light chamber (daylight $1000 \, W/m^2$, ATLAS solar constant 2500 watts HMI light, wavelengths from 350 to 1500 nm, i.e. without UV radiations, $25 \, °C$ and 50% relative humidity). They were aged up to 360 h and during ageing, samples were collected every day.

2.3. Naturally aged foams study

2.3.1. Selected samples

Among numerous naturally aged foams collected and studied, results obtained from four naturally aged flexible polyurethane foam samples ('S1' to 'S4') are reported in the present paper. Sample 'S1' was taken off from a suitcase and visually seemed to be in poor state of conservation. Sample 'S2' was sampled in a conditioning box and seemed to be in a good state of conservation. Sample 'S3' was taken off from a much degraded chair stuffing. Sample 'S4' was collected from the back of a chair (in a part not exposed to light) and obviously seemed to be in very good state of conservation. Samples 'S1' and 'S3' were very yellowed and showed total loss of coherence resulting in powdering.

2.3.2. ATR-FTIR identifications

Artificially aged modern foams as well as selected naturally aged foams of which the compositions were unknown were firstly identified using ATR-FTIR. ATR-FTIR spectra were collected using an IRTF AVATAR 360 ESP OMNI-Sampler spectrometer and a Smart accessory equipped with a single-reflection diamond ATR crystal (Thermo Electron Corporation). 128 scans were collected from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}.
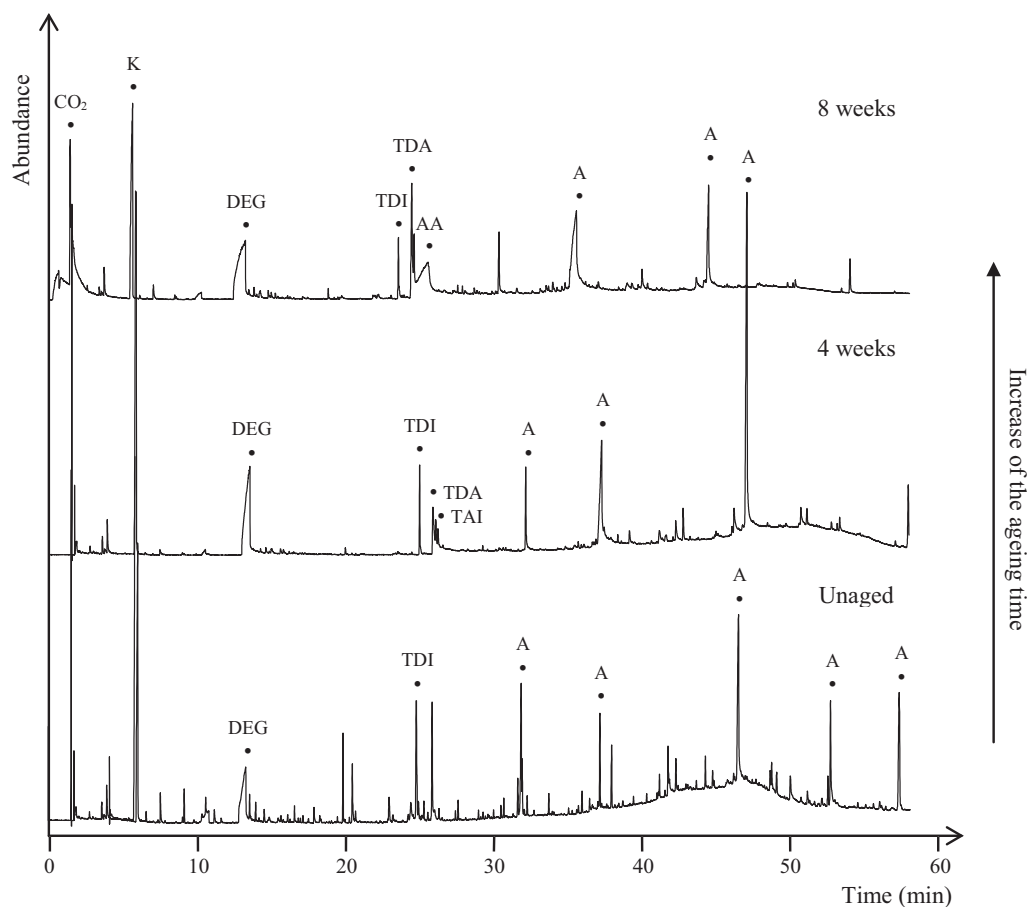
Fig. 1. Total ion chromatograms of the 650 °C pyrolyzates of modern unaged and artificially aged (in humid conditions) polyester-based polyurethane foams. For Py-GC/MS conditions, see Section 2.5. Compounds marked (•) correspond to: (K) adipic ketone, (DEG) diethylene glycol, (TDI) toluene diisocyanate isomers, (TDA) toluene diamine isomers, (TAI) toluene amino isocyanate isomers, (AA) adipic acid, (A) adipate derivatives, the chemical structures of which have not been identified with precision.

2.4. Visual examination of artificially aged modern foams and selected naturally aged foams

Visual observations and morphological changes were done by visual examinations using binocular microscope (Zeiss, Imager D2m).

2.5. Pyrolysis-GC/MS analysis

For each run, the sample was placed in a specific metal cup and the pyrolysis was performed without derivatization reagent. A new cup was used for each new sample. The pyrolysis was carried out with a Frontier Lab PY-2020iD pyrolyser and the pyrolysates were then identified using a Shimadzu GC2010 gas chromatograph coupled with a Shimadzu GCMS-QP2010Plus mass spectrometer and equipped with a pyrolysis injection system. Pyrolysis was performed at 650 °C. The pyrolyser interface was set at 320 °C. The chromatograph was equipped with a Frontier Lab UA-5 (95% dimethylpolysiloxane – 5% phenyl) fused-silica capillary column of 30 m lengh × 0.25 mm internal diameter × 0.25 μm film thickness. The oven temperature was programmed as follows: initial temperature 40 °C (hold for 1 min) increase at a rate of 10 °C min^{-1} to 180 °C and then increase at a rate of 4 °C min^{-1} to 325 °C (hold for 8 min). The carrier gas was helium with a constant flow of 1 mL min^{-1}. The split/splitless injector was used in split mode with a split ratio of 10:1 and its temperature was maintained at 280 °C. The temperatures of the interface and the source were set at 300 and 200 °C, respectively. Mass spectra were collected under electron ionization mode (EI) at 70 eV and recorded from m/z 40 to m/z

800 with a cycle time of 1 s. In order to verify the pyrolysis-GC/MS data reproducibility, three replicates runs of each artificially and naturally aged sample were performed.

2.6. HS-SPME-GC/MS analysis

2.6.1. HS-SPME sampling

In order to extract the volatile compounds, two different headspace-microextraction procedures involving different temperature and extraction time were applied, in parallel, to both the artificially and naturally aged samples: room temperature during 15 days and 60 °C during 1 h. VOCs extracted from the foam samples were then characterized using GC/MS under the same conditions, as described below (see Section 2.6.2.). For both extraction procedures, the SPME fibre used was a 50/30 μm Divinylbenzene-Carboxen/Poly(dimethylsiloxane) (DVB-CAR/PDMS) (Supelco). DVB-CAR/PDMS-coated fibre was previously shown to provide the largest qualitative distribution of VOCs extracted [57]. According to the supplier's instructions, the fibre was pre-conditioned in the GC injection port at 230 °C.

For in situ extractions performed at room temperature, the SPME fibre was placed directly in the vicinity of each naturally and artificially aged foam samples during 15 days.

For extractions performed at 60 °C during 1 h, a small piece of each naturally and artificially aged foam samples was placed in a 20 mL sample vial (Pyrex glass). The SPME fibre was inserted into the vial, a few centimetres above the sample. The vial and the fibre were then placed into a heating block (Pierce Biotechnology, France) set to the desired temperature.

Table 1
Main morphological aspects visually observed and main degradation compounds analytically characterized by Py-GC/MS and SPME-GC/MS from all the selected artificially and naturally aged foam samples.

Samples and ageing	Main morphological aspects	Main degradation compounds
Artificially aged		
Humid ageing of modern PU(ES)		
4-weeks ageing time	Slight weakening and darkening.	DEG, TDA, TAI
8-weeks ageing time	Important weakening and darkening. Presence of adipic acid crystals.	DEG, TDA, TAI, AA
Light ageing of modern PU(ET)		
120-h ageing time	Slight yellowing and cracking on the surface.	G
240-h ageing time	Important yellowing, cracking and crumbling resulting in powdering.	G
Naturally aged		
S1: PU(ES) from suitcase	Poor state of conservation: very yellowed, total loss of coherence resulting in powdering and presence of adipic acid crystals.	DEG, TDA, AA
S2: PU(ES) from conditioning box	Good state of conservation.	DEG, TAI
S3: PU(ET) from chair stuffing	Poor state of conservation: very yellowed and total loss of coherence resulting in powdering.	G
S4: PU(ET) from the back of a chair	Good state of conservation.	G

After exposure, the fibre bearing the concentrated analytes was retracted and analytes adsorbed were immediately manually injected by insertion of the fibre into the injector port of the chromatograph. Optimal desorption time and temperature were found to be 10 min at 270 °C. This time was sufficient to ensure total desorption and no memory effects (*i.e.* partial desorption) were observed, which was confirmed by desorbing the same fibre a second time after the initial desorption. The VOCs thermally desorbed were then transferred onto the gas chromatograph-mass spectrometer for identification. For each artificially and naturally aged samples, three replicates extractions were done in order to verify the SPME data reproducibility. Regardless of the type of ageing,
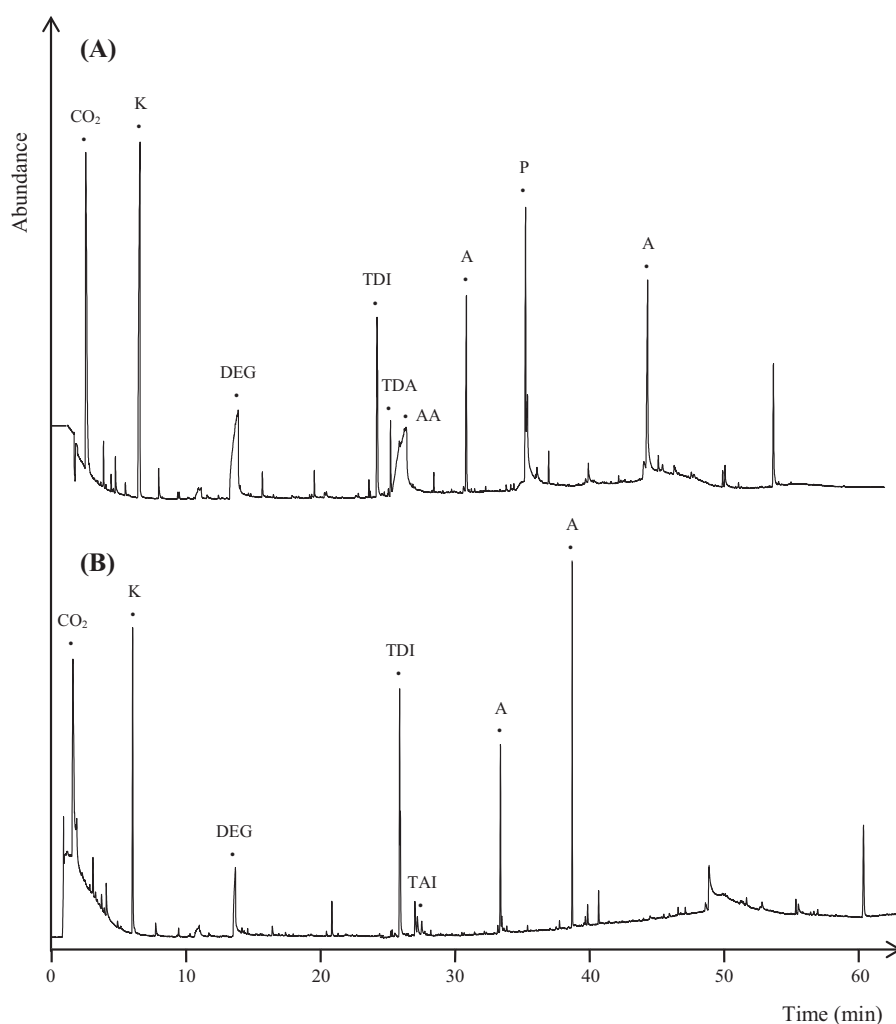

Fig. 2. Total ion chromatograms of the 650 °C pyrolyzates of naturally aged polyester-based polyurethane foams collected (A) in a suitcase 'S1′ and (B) in a conditioning box 'S2′. For Py-GC/MS conditions, see Section 2.5. Compounds marked (•) correspond to: (K) adipic ketone, (DEG) diethylene glycol, (TDI) toluene diisocyanate isomers, (TDA) toluene diamine isomers, (TAI) toluene amino isocyanate isomers, (AA) adipic acid, (A) adipate derivatives, the chemical structures of which have not been identified with precision, (P) phthalate esters.
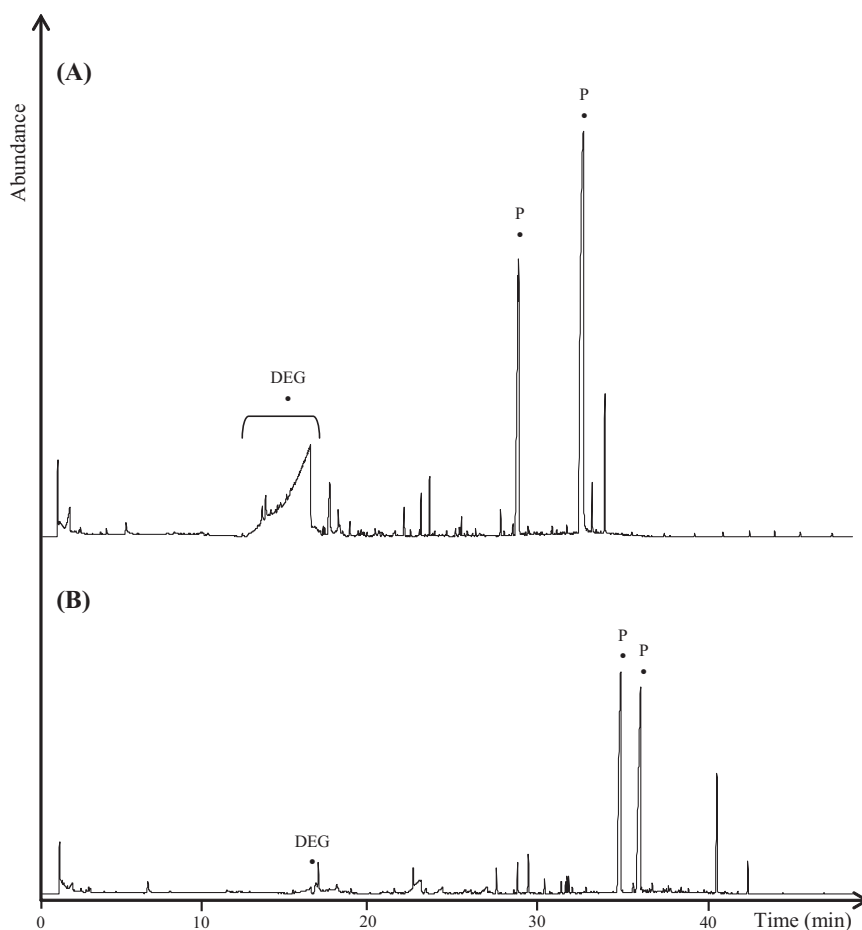
Fig. 3. Total ion chromatograms of the SPME extracts from naturally aged polyester-based polyurethane foams collected (A) in a suitcase 'S1' and (B) in a conditioning box 'S2'. For HS-SPME-GC/MS conditions, see Section 2.6. Compounds marked (•) correspond to: (DEG) diethylene glycol, (P) phthalate esters.

VOCs extracted from the foam samples were then characterized using GC/MS under the same conditions, as described below (see Section 2.6.2.).

2.6.2. HS-SPME-GC/MS analytical conditions

The volatile compounds were identified by GC/MS with a Trace GC Ultra coupled with a Trace DSQ mass spectrometer (Thermo Electron Corporation). The chromatographic peaks were identified either by direct analysis of the mass spectrum or/and comparison with a reference mass spectral library (US National Institute of Standards and Technology, NIST 02). The chromatograph was equipped with a Varian CP-Sil 8CB (95% dimethylpolysiloxane – 5% phenyl) fused-silica capillary column of 60 m length × 0.25 mm internal diameter × 0.25 μm film thickness. The oven temperature was programmed as follows: isothermal at 40 °C for 10 min, then from 40 °C to 270 °C at a rate of 5 °C min^{-1}, and isothermal hold at 270 °C for 10 min. The carrier gas was helium with a constant flow of 1 mL min^{-1}. The split/splitless injector was used in splitless mode and its temperature was maintained at 270 °C. The temperature of the interface and the source were set at 280 and 200 °C, respectively. Mass spectra were acquired under electron ionisation mode (EI) at 70 eV and recorded from m/z 33 to 600 at one cycle per second.

3. Results and discussion

3.1. ATR-FTIR analysis

Based on the literature [4,6,12,25–28] identifications performed with ATR-FTIR we could easily characterize samples 'S1' and 'S2'

as polyester-based polyurethane foams and samples 'S3' and 'S4' as polyether-based polyurethane foams. The main characteristic absorption bands (assignment, frequency and intensity) of both representative polyester-based and polyether-based polyurethane foams (made of TDI hard part) are: NH stretching of amide II and OH stretching at 3200–3300 cm^{-1} (shoulder), CH$_2$ stretching at 2800–3000 cm^{-1} (weak), NH$_2$ bending near 1600 cm^{-1} (medium) and stretching CN of amide II coupled with NH bending near 1540 cm^{-1} (strong). Besides these common bands, two main bands permit to easily distinguish between polyester-based and polyether-based polyurethane foams. They are: one strong carbonyl stretching band at 1730 cm^{-1} and one strong ether stretching band at 1180 cm^{-1} which are specific of polyester-based polyurethane foam and polyether-based polyurethane foam, respectively. Infrared spectra collected on the modern polyester-based polyurethane foam artificially aged during 8 weeks and on 'S1' sample showed, in addition to the bands specific for polyurethane on an ester basis, the presence of specific adipic acid absorption bands (C$_6$H$_{10}$O$_4$, MW 146, CAS 124-04-9). The infrared spectrum of adipic acid was previously fully assigned [60]. Its main characteristic absorption bands (assignment, frequency and intensity) are: CH stretching at 2877–2951 cm^{-1} (medium), OH stretching at 2400–2700 cm^{-1} (shoulder), carbonyl stretching at 1682 cm^{-1} (very strong), OH in plane bending at 1425 cm^{-1} (medium), C–O stretching at 1273 cm^{-1} (strong), CH$_2$ wagging at 1189 cm^{-1} (strong), OH out of plane bending at 916 cm^{-1} (strong), CH$_2$ rocking at 733 cm^{-1} (strong) and O–C–O wagging at 687 cm^{-1} (strong). Presence of this compound was verified by performing IR spectra of some white crystals samples taken directly from the
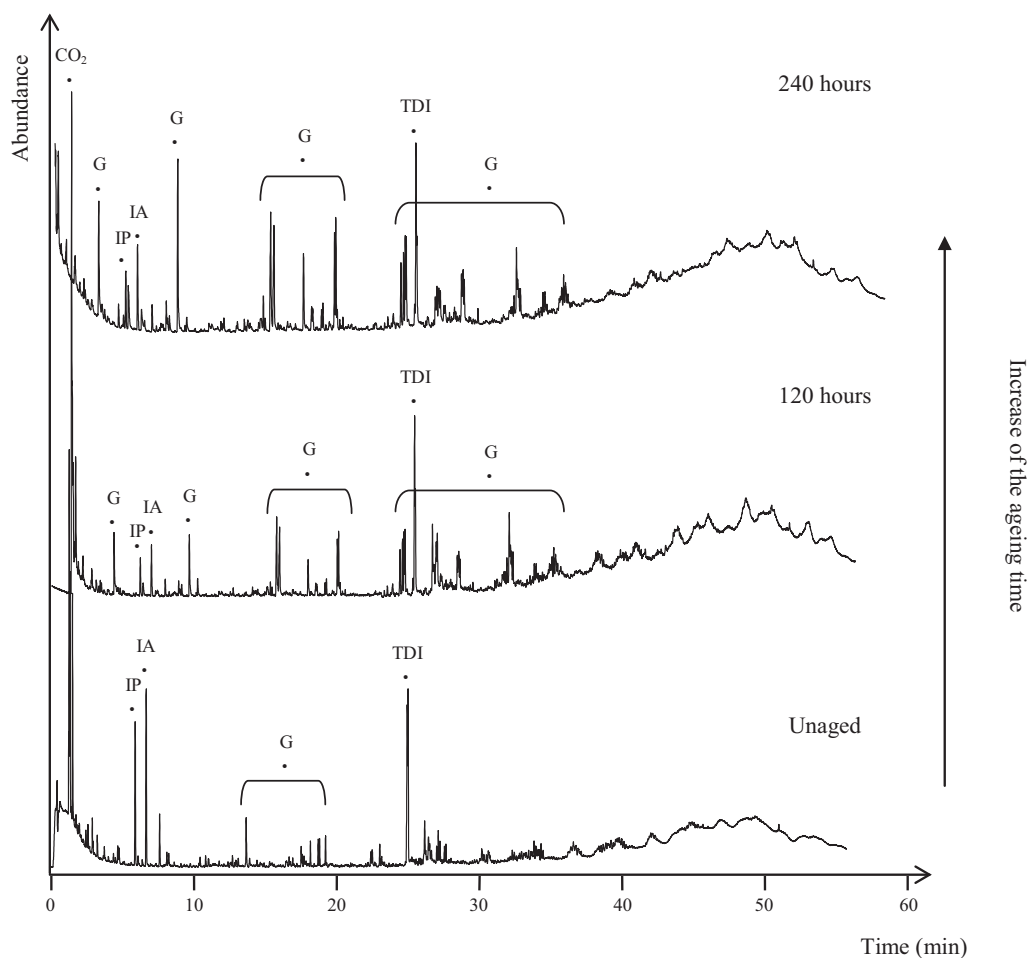
Fig. 4. Total ion chromatograms of the 650 °C pyrolyzates of modern unaged and artificially aged (upon light conditions) polyether-based polyurethane foams. For Py-GC/MS conditions, see Section 2.5. Compounds marked (•) correspond to: (IP) 1-propoxypropan-2-ol, (IA) propoxyacetone isomer, (TDI) toluene diisocyanate isomers, (G) glycol derivatives, the chemical structures of which have not been identified with precision.

pores or from the surface of both foam samples. Such crystals have been previously detected and identified from one PU artefact. In agreement with the authors, its occurrence demonstrated that polyester-based polyurethane foam can be hydrolysed into its raw materials [3,4,9]. These samples proved to be polyester-based polyurethanes.

3.2. Visual examination of artificially aged modern foams and naturally aged foams

As illustrated by previous works [9,12,16], the main morphological change observed in the modern polyester-based polyurethane samples was the very fast weakening and darkening of the foam during ageing in humid conditions. More precisely, the modern polyurethane ester foam sample artificially aged in humid conditions during 4 weeks showed slight weakening and darkening. After 8 weeks of ageing, an important weakening and darkening as well as some white adipic acid crystals inside the pores and on the surface of the foam were observed. This result completed previous work [9] and demonstrated that the artificial degradation of polyester-based polyurethane foam in an open environment can lead to the formation of adipic acid. White adipic acid crystals were also observed on 'S1' naturally aged. Regarding modern polyether-based polyurethane foam samples, the main changes were observed with light ageing. Photo-oxidation causes chain scission and yellowing, cracks and crumbling (i.e. loss of coherence) often starting at the surface skin of the foams and resulting in pow-

dering and leading, in some cases, to the complete destruction of the samples [12,14,16]. More precisely, the 120-h aged sample showed a slight yellowing and some crakes on its surface. After 240 h of ageing, we observed yellowing, cracking and crumbling resulting in powdering. Same typical degradations were noted on the 'S3' naturally aged sample from the chair stuffing. The main morphological aspects visually observed from the artificially and naturally aged samples are gathered in Table 1.

3.3. Pyrolysis-GC/MS and HS-SPME-GC/MS analysis of artificially and naturally aged polyester-based polyurethane foams

3.3.1. Pyrolysis-GC/MS analysis

Pyrolysis mechanisms and thermal behaviour of polyurethane polymers have been extensively studied by others. They suggested that there are three main pathways for the initial degradation of the polyurethane linkage [21–24,29–35]. Our objective was neither to suggest decomposition pathways for the pyrolysis degradation of polyurethane foams nor was to provide optimised analytical protocol for their analyses. As previously reported, the pyrolyzates distribution of the polyurethane depends on the analytical parameters and strongly on the pyrolysis temperature. In the present research, we applied same standard analytical conditions for all artificially and naturally aged foams. These conditions gave PU foam fingerprints that permitted identifying potential chemical markers of the PU foam degradations.
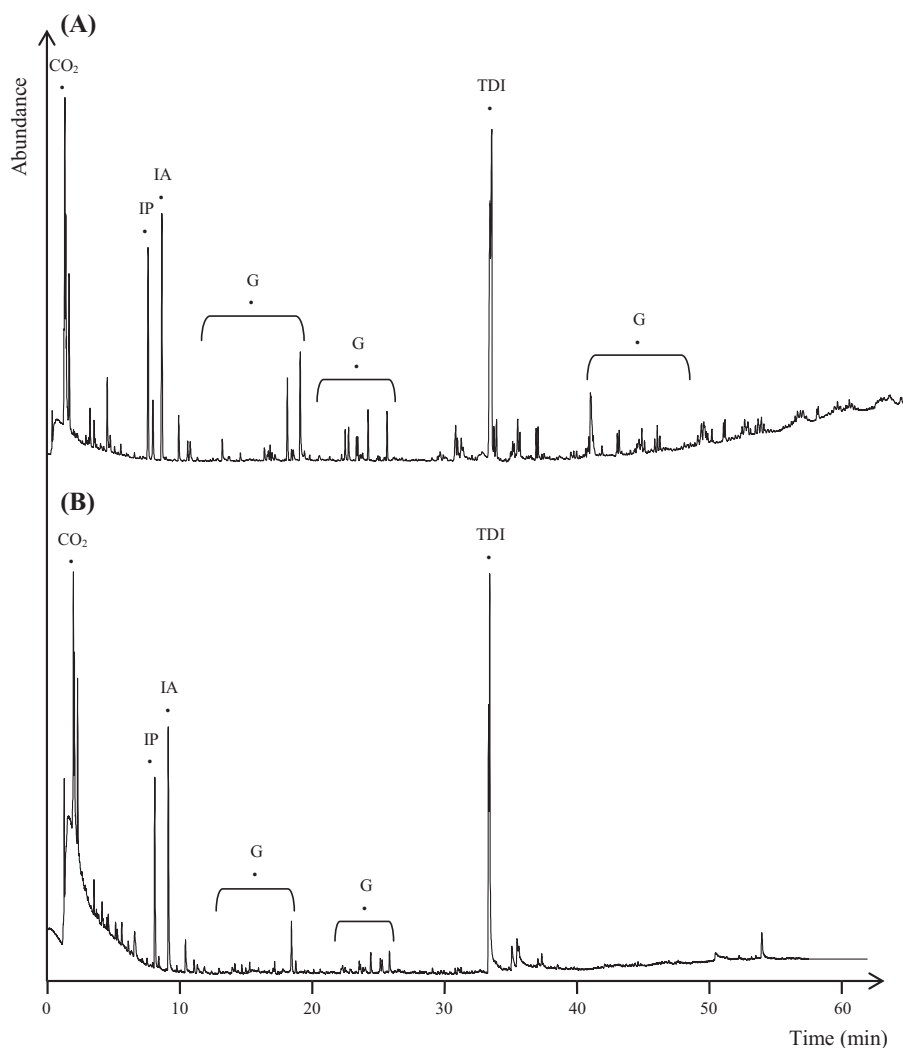
Fig. 5. Total ion chromatograms of the 650 °C pyrolyzates of naturally aged polyether-based polyurethane foams collected (A) in a chair stuffing 'S3' and (B) in the back of a chair 'S4'. For Py-GC/MS conditions, see Section 2.5. Compounds marked (●) correspond to: (IP) 1-propoxypropan-2-ol, (IA) propoxyacetone isomer, (TDI) toluene diisocyanate isomers, (G) glycol derivatives, the chemical structures of which have not been identified with precision.

Fig. 1 shows the total ion chromatograms (TICs) of the 650 °C pyrolyzates of modern polyurethane ester foam samples unaged and artificially aged in humid conditions during 4 and 8 weeks. These two ageing times were selected because pyrograms showed relevant modifications. But, it's obvious that these durations are specific to this work and are just indicative of the increase of the ageing.

From the unaged sample, few compounds (marked with a black dot) were identified. They were: carbon dioxide, adipic ketone (K), diethylene glycol (DEG), 2,4- and 2,6-toluene diisocyanate isomers (TDI) and some adipate derivatives (A) of which chemical structures have not been identified with precision. As previously suggested, adipic ketone (C_5H_8O, MW 84, CAS 120-92-3) can originate from the adipic acid raw material [33,35]. Concerning DEG ($C_4H_{10}O_3$, MW 106, CAS 111-46-6), this low molecular weight polyol can be used in the polyurethane fabrication either as chain extenders (*i.e.* low molecular weight reactants that produce the familiar elastomeric properties of the polyurethanes) or for the polyester polyol synthesis. 2,4- and 2,6-TDI isomers respectively ($C_9H_6O_2N_2$, MW 174, CAS 584-84-9 and 91-08-7) are issued from the primary scission of the urethane linkage and the ester bond leading to the formation of isocyanate and alcohol [21–24]. TDI is most commonly used isocyanate for flexible foams.

When ageing time increased, chromatographic fingerprints got simple and, the isocyanate hard part was modified. After 4 weeks of ageing, in addition to the relative increase of diethylene glycol, we noted the occurrence of toluene amino isocyanate isomers (TAI) and 2,4- and 2,6-toluene diamine isomers (TDA). Compounds assigned TAI could be toluene amino isocyanate isomers formed by partial hydrolysis of TDI [61]. 2,4- and 2,6-toluene diamines are issued from the hydrolysis of TDI isomers. An increasing release of 2,4- and 2,6-TDA with increasing duration of 2,4- and 2,6-TDI hydrolysis have been previously reported [62]. Such compounds could be linked to the dissociation of isocyanate to primary amine, second main pathways for the degradation of the urethane linkage [21–24].

After 8 weeks of ageing, adipic acid was identified. In agreement with the literature, Py-GC/MS data showed that by hydrolysis, polyester polyol reverses to the precursor dicarboxylic acid and polyol used for its synthesis. This precursor acid further catalyzes ester hydrolysis, and thus becomes autocatalytic. Flexible polyester-based polyurethane foams are often primarily adipate ester of diols. More precisely, they are obtained by polyesterification between adipic acid and diols such as diethylene glycol [17]. The research done in the last few years proved that high hydrophobicity of the glycol or dicarboxylic acid, low concentration
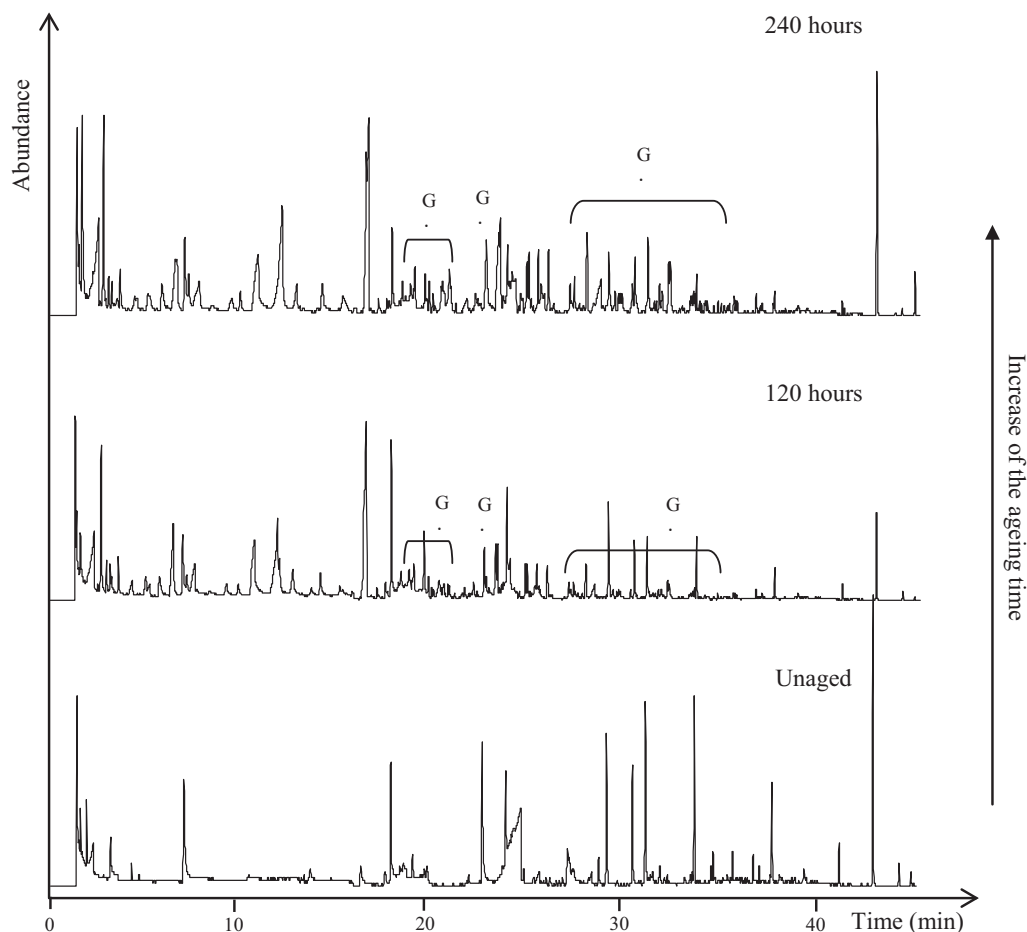
Fig. 6. Total ion chromatograms of the SPME extracts from modern unaged and artificially aged (upon light conditions) polyether-based polyurethane foams. For HS-SPME-GC/MS conditions, see Section 2.6. Compounds marked (•) correspond to: (G) glycol derivatives, the chemical structures of which have not been identified with precision.

of ester bonds, low polyester polyol acidity and high steric hindrance around the ester group confer hydrolysis resistance to the polyester-based PU. Considering these factors, it has been established that poly(diethylene glycol adipate) polyurethanes have a poor hydrolytic stability. Since toluene diamine isomers and adipic acid did not appear after thermal dry ageing, their occurrences confirmed that polyester-based PU foams are liable to hydrolysis.

Fig. 2 presents two Py-GC/MS fingerprints of foams naturally aged which were obviously in different states of conservation. These fingerprints were very representative of all naturally aged foams collected in different places and very similar with those obtained for the modern polyester-based foam upon artificial ageing. Firstly, thanks to pyrograms previously obtained from the modern samples, it was easy to identify these two foams such as poly(diethylene glycol adipate) polyurethanes. Phthalate derivatives (*e.g.* phthalic acid diisobutyl ester) could come from plasticizers introduced during the manufacturing process. Secondly, sample 'S1′ revealed the presence of a relatively high amount of diethylene glycol (DEG), of 2,4- and 2,6-toluene diamines (TDA) and of adipic acid (AA). Pyrogram of the foam 'S2′ which was in good state of conservation showed a relative lower amount of diethylene glycol (DEG), presence of toluene amino isocyanate isomers (TAI) and no trace of adipic acid. These results were coherent with those obtained from artificial ageing and therefore the presence of these compounds can be considered as degradation markers.

To sum up, the good match between natural ageing and artificial humid ageing confirmed that the dominant environmental factor on PU(ES) foam deterioration is hydrolysis.

3.3.2. HS-SPME-GC/MS analysis

To assess the relevance of HS-SPME-GC/MS method for trapping and identifying non-invasively (*i.e.* without any sampling on the foams themselves) polyurethane foam emissions, in situ SPME extraction procedure was tested on all the selected naturally and artificially aged foam samples. The fibre was placed directly in the vicinity of the foam sample at room temperature during 15 days. These conditions were chosen as a good compromise between sensitivity and analysis time since it has already been shown that a shorter time is not sufficient to accumulate a large number of VOCs and a longer time does not increase the extraction efficiency [57]. In parallel, for practical reasons, SPME extractions were also performed on all the same samples at 60 °C during 1 h. Such extractions required to sample a small piece from all selected foams and thus cannot be considered as a non-invasive sampling methodology. Whichever the extraction procedure, qualitative data obtained at room temperature during 15 days and by extraction at 60 °C during 1 h were very similar: the same compounds were eluted. However, chromatograms of the in situ SPME extracts from both naturally and artificially aged showed some noisier background linked to the presence of environmental pollutants. For artificially and naturally aged polyester-based polyurethane foams as well
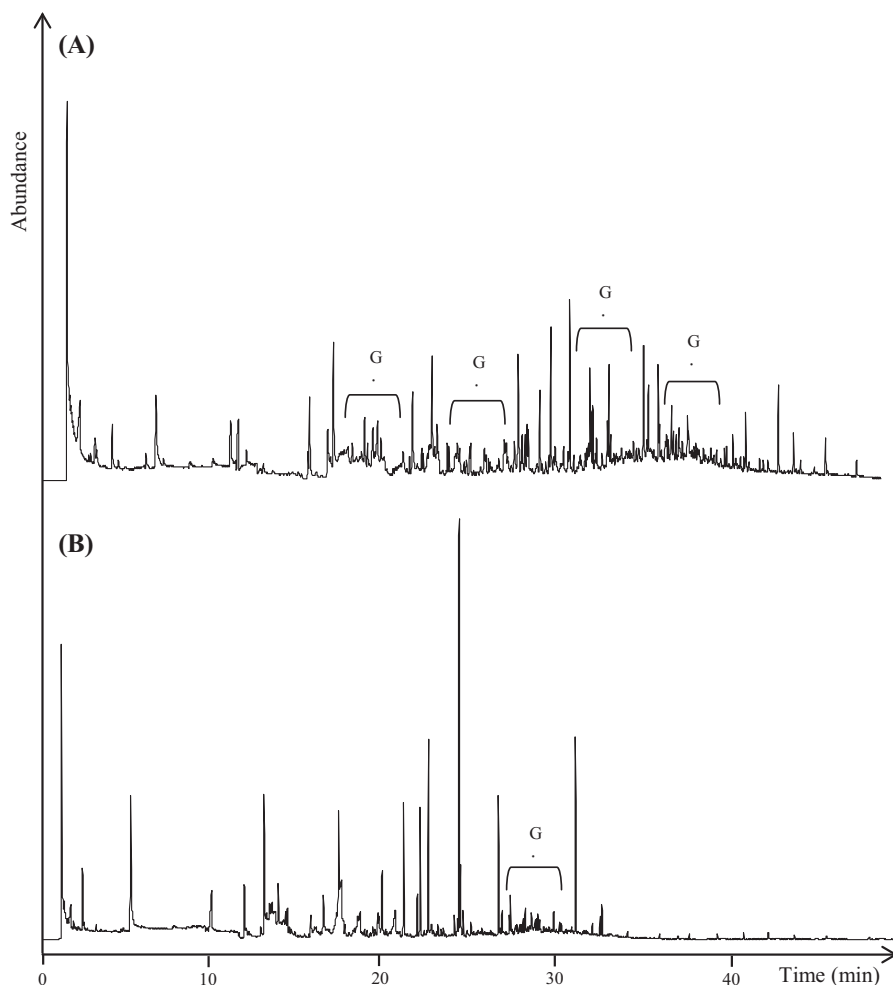
Fig. 7. Total ion chromatograms of the SPME extracts from naturally aged polyether-based polyurethane foams collected (A) in a chair stuffing 'S3' and (B) in the back of a chair 'S4'. For HS-SPME-GC/MS conditions, see Section 2.6. Compounds marked (•) correspond to: (G) glycol derivatives, the chemical structures of which have not been identified with precision.

as for artificially and naturally aged polyether-based polyurethane foams, we will present in this article the analytical results obtained with HS-SPME, an invasive extraction procedure (at 60 °C and 1 h). Chromatograms of the SPME extracts from the modern ester foam artificially aged in humid conditions did not indicate the obvious changes within the VOCs composition but the presence of diethylene glycol (DEG). TICs of the SPME extracts from all naturally aged PU(ES) foams collected in different places were very similar. The presence in different relative amount of diethylene glycol was noted. Fig. 3 presents two representative SPME fingerprints from foams 'S1' and 'S2' which were in different states of conservation. Firstly, we noted that whatever the state of conservation was, non-invasive SPME-GC/MS analysis enabled us to conclude that these foams are made up of poly(diethylene glycol ester) polyurethanes. Secondly, the relative increase of diethylene glycol could be correlated with the physical state of the foams. It could be used as a volatile marker of the foam degradation. Some intense phthalates esters, the chemical structures of which have not been identified with precision, were also observed. They cannot be considered as characteristic of PU(ES). Toluene diisocyanate isomers, toluene diamine isomers, toluene amino isocyanate isomers and adipic acid are not volatile compounds in the conditions of extraction used.

From Py-GC/MS and HS-SPME-GC/MS approaches, it seems relevant to further apply such accelerated humid ageing to simulate natural degradation processes of PU(ES) foams.

The main morphological aspects visually observed and the main degradation compounds analytically characterized from the artificially and naturally aged polyester-based polyurethane foam samples are summarized in Table 1.

3.4. Pyrolysis-GC/MS and HS-SPME-GC/MS analyses of artificially and naturally aged polyether-based polyurethane foams

3.4.1. Pyrolysis-GC/MS analysis

Fig. 4 shows the total ion chromatograms of the 650 °C pyrolyzates of modern polyurethane ether foam samples unaged and artificially aged with light for 120 and 240 h. These two ageing times were selected because pyrograms showed relevant modifications.

From the unaged sample, few compounds (marked with a black rod) were indentified. They were: carbon dioxide, 1-propoxypropan-2-ol (IP), one isomer of propoxyacetone (IA), 2,4- and 2,6-toluene diisocyanate isomers (TDI) and some glycol derivatives (G) of which chemical structures have not been identified with precision. Pyrogram obtained was very different from the one of the unaged modern polyester foam. It was very easy to distinguish between PU(ES) and PU(ET). 1-propoxypropan-2-ol ($C_6H_{14}O_2$, MW 118, CAS 1569-01-3) and isomer of propoxyacetone ($C_6H_{12}O_2$, MW 116) are both involved in the manufacturing of polyurethane foams. 2,4- and 2,6-TDI isomers are issued from the breakdown of the urethane linkage and the polyether

polyol part. Compounds with glycol chemical structures (G) were mainly identified as ethylene glycol, propylene glycol, dipropylene glycol, tetrapropylene glycol and their monomethyl ether derivatives.

During ageing, as illustrated by pyrograms obtained after 120 and 240 h, we noted no obvious modification of the isocyanate hard part. Conversely, relative amount of compounds with glycol chemical structures significantly increased. Polypropylene glycol, one of the most important polyether polyols used in polyurethane formulation is formed by the polymerisation reaction of a cyclic ether such as propylene oxide (or mixture of propylene oxide and ethylene oxide) initiated by a bifunctional starter such as propylene glycol [17]. Glycol derivatives are breakdown products produced during artificial light ageing of the polyether polyol soft part. Such compounds were not detected after thermal ageing. These results confirmed that the hydrolysis resistance of PU(ET) is far better than that of PU(ES) and that polyether-based PU foams are very sensitive to photo-oxidation.

Fig. 5 presents two Py-GC/MS fingerprints of foams naturally aged 'S3′' and 'S4′' which were in different states of conservation. These pyrograms were very representative of all naturally aged foams collected in different places and very similar with those obtained for the modern polyether-based foam upon ageing. Firstly, by comparison with pyrograms previously obtained, it was easy to identify these two foams as polyether(polypropylene glycol)-based polyurethane foams. Secondly, foam in good condition 'S4′' showed a pyrogram very similar to the one of the unaged modern PU(ET). It presented a very low relative amount of glycol derivatives. From the foam in bad condition 'S3′', we noticed a pyrogram very similar to the one of the modern PU(ET) foam after artificial light ageing. It showed the presence of a relatively high amount of breakdown products that could be considered as markers of the state of the foam degradation.

To sum up, the good match between natural and artificial light ageing permitted to confirm that the dominant deterioration path for PU(ET) foam is photo-oxidation.

3.4.2. HS-SPME-GC/MS analysis

Chromatograms of the SPME extracts from the modern polyurethane ether foam artificially aged with light conditions (Fig. 6) indicated the increase of glycol derivatives with the ageing time. TICs of the SPME extracts from all naturally aged PU(ET) foams collected in different places were very similar. The presence in different relative amount of diethylene glycol was noted. Fig. 7 presents two representative SPME fingerprints from the foams 'S3′' and 'S4′'. Firstly, we noted that whatever the state of conservation was, non-invasive SPME-GC/MS analysis enabled us to identify these foams as polyether-based polyurethane foams. Secondly, the relative increase of the amount of glycol derivatives could be correlated with the physical state of the foams. These compounds could be used as volatile markers of the degradation of the foam. From the Py-GC/MS and HS-SPME-GC/MS approach, it seems relevant to further apply such accelerated light ageing to simulate natural degradation processes. The main morphological aspects visually observed and the main degradation compounds analytically characterized from the artificially and naturally aged polyether-based polyurethane foam samples are summarized in Table 1.

4. Conclusions

The aim of this research was to assess the degradation of some artificially and naturally aged polyurethane foams. One modern polyester-based polyurethane foam subjected to artificial humid ageing, one modern polyether-based polyurethane foam subjected to artificial light ageing and some naturally aged foams collected from to day objects in different uncontrolled environmental places were investigated by using visual examinations, Py-GC/MS and HS-SPME-GC/MS. It showed that main degradation compounds formed upon natural and artificial ageing are alcohol and acid raw material for PU(ES) and glycol derivatives for PU(ET). These degradation products can be considered as degradation markers for PU foams. It is interesting to note that, in this study, artificial and natural ageing were providing similar analytical results and thus, it seems relevant to apply such accelerated ageing to simulate natural degradation processes. These results confirm that the dominant degradation path for polyurethane foams degradation is hydrolysis in the case of PU(ES) and photo-oxidation for PU(ET). Lastly, it has also been shown that it is possible to distinguish between PU(ES) and PU(ET) at any point of degradation using non-invasive HS-SPME-GC/MS analysis.

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