# A pyrolysis approach for characterizing and assessing degradation of polyurethane foam in cultural heritage objects

Jacopo La Nasa[a], Greta Biale[a], Barbara Ferriani[b,c], Maria Perla Colombini, Francesca Modugno[a]*

[a]Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy
[b]Conservation Laboratory at the Triennale Design Museum, Milano, Italy
[c]Barbara Ferriani S.r.l., Milano, Italy
*: francesca.modugno@unipi.it

**Abstract**

Specific analytical tools are needed to investigate the composition and degradation processes of the synthetic materials in the cultural heritage, and recent advancements in pyrolysis-based analytical techniques have great potential for the characterisation of synthetic polymers. We applied evolved gas analysis mass spectrometry (EGA-MS) and double shot pyrolysis coupled with chromatography and mass spectrometry (Py-GC/MS) to investigate polyurethane foam micro-samples from the Italian pop-art sculpture "Contenitoreumano n.1" (1968) by Ico Parisi (1916-1996) and Francesco Somaini (1926-2005). The chemical analysis aimed to assess the chemical composition and of the state of preservation of the PU foam by acquiring information on its thermal degradation behaviour and identifying the pyrolysis products produced at different temperatures. A preliminary ATR-FTIR analysis was also carried out. The multi-analytical approach enabled us to identify the isocyanate and polyol precursors as 2,6-toluenediisocyanate and polypropylene glycol, respectively. The plasticizers used in the production of the PU foam were also identified in the first shot of a double shot Py-GC/MS experiment. A comparison of a sample of better preserved foam with a sample of degraded foam from the surface of the object highlighted that the more degraded part of the PU foam featured an increase in the thermal degradation temperature of the soft-fragments of the PU network, related to cross-linking phenomena. Moreover, loss of plasticizers and formation of NH2 functional groups was observed in the degraded foam.

**Keywords**

Polyurethane foams, Cultural Heritage Objects, Degradation processes; Analytical Pyrolysis, Evolved Gas Analysis

## 1. INTRODUCTION

The 20th century witnessed a revolution in the composition of artists' materials. Today, modern and contemporary collections face challenging conservation issues related to the wide variety of synthetic polymer-based plastics present in art and design collections [1,2].

To preserve the stability of synthetic polymeric materials, some of which were not intended to last longer than a few decades after their production, specific analytical tools are required for their identification, to investigate the degradation processes, and to assess the preservation state of specific objects. In this context, analytical pyrolysis is emerging as a fundamental tool for the analysis of polymers in heritage science [3-10], also thanks to recent developments such as evolved gas analysis mass spectrometry (EGA-MS) and multi-shot pyrolysis coupled with chromatography and mass spectrometry (multi-shot Py-GC/MS). These techniques have only been applied in heritage studies in a few cases, but have shown a good potential in the investigation of synthetic paint binders [11-14], archaeological wood [15], and conservation materials such as wood consolidants [16], lacquers [17], and proteinaceous residues [18].

Of the synthetic polymers encountered in 20th century artworks and design objects, polyurethane was first synthetized in 1937 in Germany. However, it was only in the late 1960s, as a consequence of the widespread use of polyurethane in the industrial production of everyday objects, that artists approached this new material attracted by its peculiar and innovative features, as lightness and softness [19,20]. Polyurethanes can also be found as a constituent of works of art such as rigid and flexible foams in design objects and sculptures [21]. Today conservators are faced with the limited durability of polyurethane foams which affects the stability of the artworks. In fact, the first polyurethanes began to degrade only a few decades after their production [20,21]. The limited knowledge available on the degradation of polyurethane foams, along with the wide variety of possible compositions for these materials, make the degradation of PU foams a critical conservation issue [20,21] .

Infrared spectroscopic techniques have proven efficient in characterising different classes of polymers including PU [22-27].

However a detailed molecular analysis and the identification of specific monomeric precursors require a micro-invasive characterisation of samples, which is possible by Py-GC/MS [20,28,29].

EGA-MS, which has shown promising results in the analysis of polyurethanes [30], and combined with multi-shot Py-GC/MS has great potential in the selective characterisation of plastic components on the basis of their thermal decomposition behaviour.

In this work, we evaluated a combination of EGA-MS and double shot Py-GC/MS in the investigation of a polyurethane foam sculpture pertaining to Italian pop art, "Contenitoreumano n.1" (1968) by Ico Parisi (1916-1996) and Francesco Somaini (1926-2005), which is shown in Figure 1. The chemical analysis of the foam constituting the object, which could be ambiguously classified both as an artwork

and as the prototype of a piece of design furniture, took place before a conservation intervention performed by Triennale Design Museum of Milan in 2017 [31]. A preliminary ATR-FTIR analysis was also carried out [8,9,32]. Micro-samples of PU foam with different states of preservation were examined, in order to obtain a picture of the chemical composition and of the degradation processes of the PU, based on its thermal degradation behaviour. The two pyrolysis-based approaches were applied in this study for the first time in the characterisation of PU in cultural heritage.

Figure 1. The Contenitoreumano n.1 by Ico Parisi and Francesco Somaini, 1968, metal and polyurethane foam, 1250 x 1575 x 92 cm, in a historical photograph (left) and after the 2017 conservation intervention. Photo: Triennale Design Museum (Milan).

## 2. MATERIALS AND METHODS

### 2.1 Investigated materials and samples

The investigated object, dated 1968, is one of the two existing prototypes of Contenitoreumano n.1 by Ico Parisi and Francesco Somaini, originally consisting of a metallic case painted white with handles on both sides, on which the words "Contenitoreumano" were written in red followed by the authors' names. The name of the prototype series could be translated as "Human receptacle" or "Human container", and the series was intended as a utopian reflection on human inhabitation [31]. This shell contained a soft internal structure created by the juxtaposition of various layers of molded polyurethane foam, equipped with plastic tubes imagined delivering food and drink to the person inside (Figure 1). The prototype was restored at the Conservation Laboratory of the Triennale Design Museum of Milan in 2017. The sampling and analysis were carried out within the framework of the IPERION CH.it project "Plastic in the collection of the Triennale Design Museum in Milan". Micro-sampling followed by laboratory analysis was selected as the investigation approach because a non-

invasive characterization by a portable in situ spectrophotometric technique was not possible for this porous material.

Two fragments of polyurethane foam from the artwork were collected (around 2 mg each, corresponding to few $mm^3$ of foam): one from the bulk of the foam, identified as CU3, which appeared to be less degraded, and the other fragment from the external surface of the foam, identified as CU4, which showed a certain degree of yellowing, and was more rigid and brittle than the bulk material. The two fragments were directly examined by ATR-FTIR, and then sub-sampled for EGA-MS and Py-GC/MS micro-destructive analysis.

## 2.2 Optical microscopy

Optical microscopy images of the foam fragments were acquired using an Olympus BX51M optical microscope equipped with fixed oculars of ×10, and lenses with ×5 magnification (the other possible magnifications are ×10, ×20, ×50 and ×100) for dark field observations. The instrument was equipped with a 100 W halogen projection lamp for visible light acquisition, and with an Olympus U-RFL-T lamp for visible fluorescence acquisition. The images were recorded with a digital scanner camera Olympus XC50 directly connected to the microscope.

## 2.2 Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra were collected directly on fragments of foam using a Perkin Elmer Spectrum 100 spectrometer coupled with a MIRacle TM ATR accessory equipped with a SeZn crystal. Sixteen scans were collected from 4000 to 650 $cm^{-1}$ with a resolution of 4 $cm^{-1}$. The analyses were performed at room temperature (22°C). Jasco Spectra Manager software was used for data analysis.

## 2.3 Evolved gas analysis-mass spectrometry

The samples were placed into a pyrolysis stainless-steel cup, weighted, and inserted into the microfurnace. The weight of samples was CU3 and CU4 were 106 µg and 98 µg respectively. The instrumentation consisted of a micro-furnace Multi-Shot Pyrolyzer EGA/Py-3030D (Frontier Lab, Japan) coupled with a gas chromatograph oven 6890 Agilent Technologies (USA) kept at 300C°, connected with a mass the Mass Selective Detector single quadrupole mass through an Ultra ALLOY ® EGA Tube (2.5 m x 0.15 mm i.d).

Temperature program for the micro-furnace chamber of the pyrolyzer: initial temperature 50 °C; 10 °C/min up to 800 °C for 10 minutes. Analyses were performed under a helium flow (1 ml/min) with a split ratio 1:20. The micro-furnace interface temperature was automatically kept at 100 °C higher than the furnace temperature up to the maximum value of 300 °C. The inlet temperature was 280 °C. The mass spectrometer was operated in EI positive mode (70 eV, scanning m/z 50-700). The MS transfer

line temperature was 300 °C. The MS ion source temperature was kept at 230 °C, and the MS quadrupole temperature at 150 °C. A scheme of the analytical set-up is shown in Figure 2a.

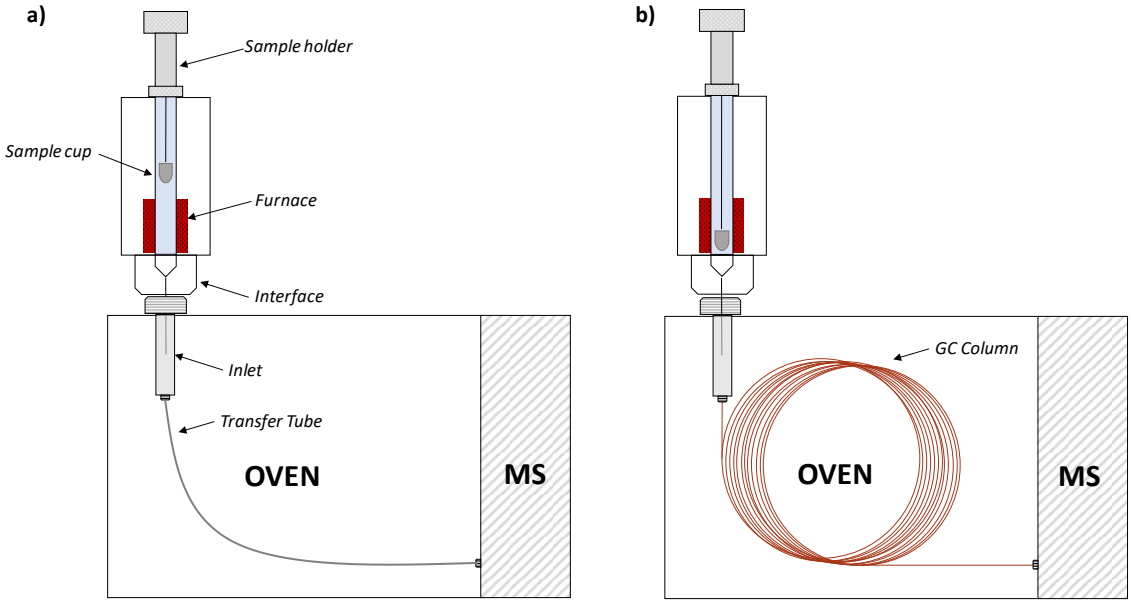



**Figure 2** Instrumental asset of the Frontier Lab Multi-Shot Pyrolyzer EGA/Py-3030D used for a) evolved gas analysis/mass spectrometry (EGA-MS) and b) multi-shot pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) .

## 2.4 Multi-shot pyrolysis-gas chromatography/mass spectrometry

Analyses were performed using a multi-shot pyrolyzer EGA/PY-3030D (Frontier Lab) coupled with a 6890N gas chromatography system with a split/splitless injection port, and with a 5973 mass selective single quadrupole mass spectrometer (both Agilent Technologies) [33], as shown in Figure 2b.

The samples were placed in stainless-steel cups and the sample weights were CU3 and CU4 were 56 µg and 60 µg respectively. Multi-shot pyrolysis conditions were optimized as follows: pyrolysis temperatures were selected based on the specific EGA/MS results for each sample: the first shot was performed at 306°C and the second at 600°C.

interface 280 °C. The GC injector temperature was 280 °C. The GC injection was operated in split mode with a split ratio of 1:10. The chromatographic separation of pyrolysis products was performed on a fused silica capillary column HP-5MS (5% diphenyl-95% dimethyl-polysiloxane, 30 m x 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific, Agilent Technologies), preceded by 2 m of deactivated fused silica pre-column with an internal diameter of 0.32 mm. The chromatographic conditions were: 40 °C for 5 min, 10 °C/min to 310 °C for 20 min. The helium (purity 99.9995%) gas flow was set in constant flow mode at 1.2 mL/min [7-9,34-36].

MS parameters: electron impact ionization (EI, 70 eV) in positive mode; ion source temperature 230 °C; scan range 50-700 m/z; interface temperature 280 °C. Perfluorotributylamine (PFTBA) was used for mass spectrometer tuning. MSD ChemStation (Agilent Technologies) software was used for data

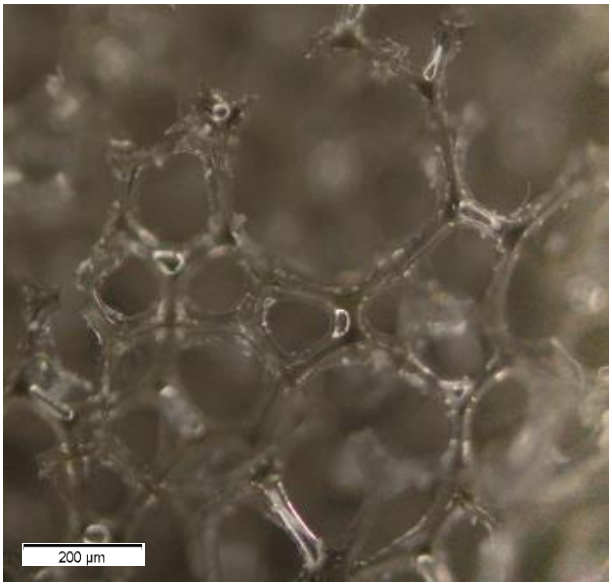
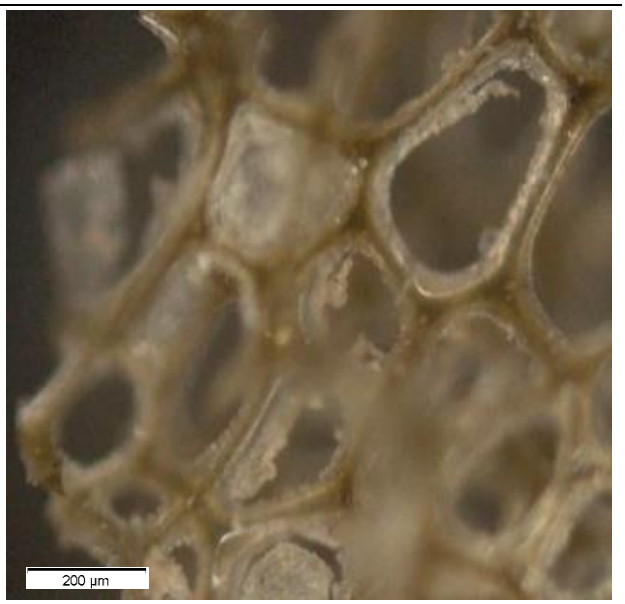
analysis and the peak assignment was based on a comparison with libraries of mass spectra (NIST 1.7, WILEY275) and the literature data [29].

## 3. RESULTS AND DISCUSSION

### 3.1 Optical microscopy

The microscopic comparison of the better preserved and the more degraded samples from Contenitoreumano (Table 1) showed damage of the polymeric cell-like structure in the sample CU4 from the surface of the object. The materials also appeared more yellow and darkened compared to sample CU3. Yellowing is a significant indicator of chemical changes in polymers containing aromatic structures, and it can be expected to occur as a result of the formation of additional double bonds conjugated with the aromatic ring [37].

**Table 1** Investigated samples from "Contenitoreumano n.1" and optical microscopy images.

| Sample | Optical microscopy |
|---|---|
| CU3<br>Bulk foam,<br>better preserved |  |
| CU4 Surface foam,<br>significantly degraded |  |

### 3.2 ATR-FTIR

Figure 3 shows the ATR-FTIR spectra of samples CU3 (bulk) and CU4 (surface). The identification of the observed ATR-FTIR bands is reported in Tables 2 and 3 for samples CU3 and CU4, respectively [19,38-42].

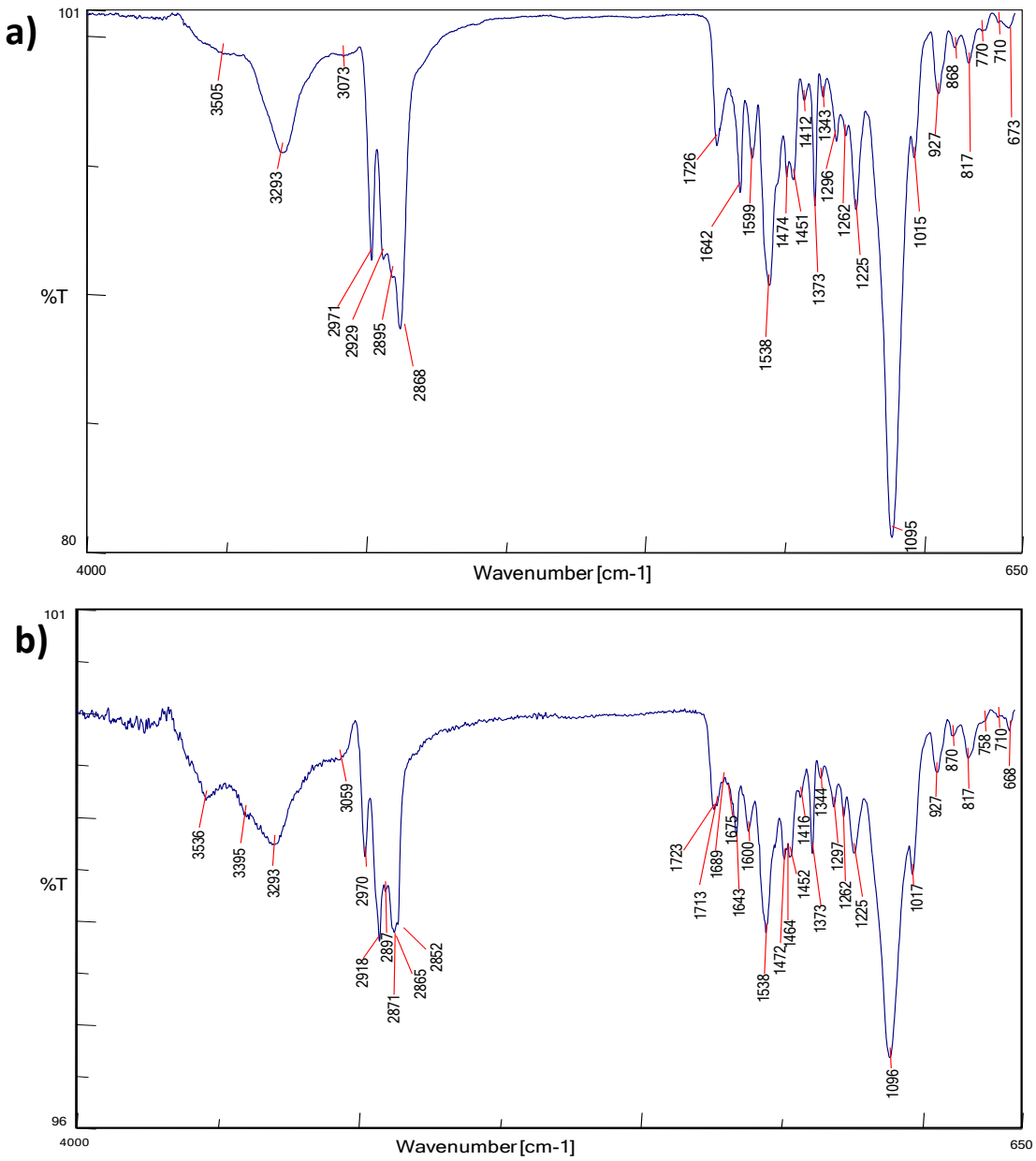



**Figure 3** ATR-FTIR spectra obtained for the samples: a) CU3 (bulk) and b) CU4 (surface) from "Contenitoreumano n.1". The band assignments are reported in Tables 2 and 3.

ATR-FTIR shows that the polyurethane used in "Contenitoreumano n.1" is a polyether-based polyurethane. The polyether-based polyol marker is the asymmetric stretching vibration of C-O-C at 1095 $cm^{-1}$. PUs are also strongly self-associated through intermolecular hydrogen bonding [43]. The hydrogen bonding interactions are formed between the hard segments of the polyurethane and consist in the physical crosslink of PUR flexible foams (virtual crosslink). Studies have demonstrated that these interactions act as a covalent bonding at room temperature, and are significant in the

determination of PU properties [44]. The absorption bands related to hydrogen bond interactions are: 3661-3434 $cm^{-1}$ (stretching vibration of non-H-bonded N-H), 3293 $cm^{-1}$ (stretching of H-bonded N-H), 1723-1726 $cm^{-1}$ (stretching vibration of non H-bonded urethane), and the carbonyl band at 1630-1730 $cm^{-1}$. Other significant regions are between 3000 and 2850 $cm^{-1}$ (-C-$H_3$ and -C-$H_2$ stretching) and between 930 and 600 $cm^{-1}$, which includes the bending of C-H benzene rings and the -C-$H_2$ skeletal deformations.

To highlight spectral changes related to the deterioration of the polyurethane foam, the two spectrums of the better-preserved bulk sample (CU3) and the more degraded surface sample (CU4) were compared. The main differences between the PU portion with different state of preservation were observed evaluating the N-H, C-H and C=O (amide I) stretching regions, comparing relative intensities of bands in the same spectra. The surface sample CU4 showed a changing in the relative intensity of the broad band between 3661 and 3000 $cm^{-1}$. In this region N-H stretching vibration bands occur, together with a band at approximately 3395 $cm^{-1}$ which can be attributed to the formation of quinone-imides with hydroperoxides as intermediates [45]. These products, along with the decrease in the relative intensity of the C-O-C band, suggest the partial scission of the soft segment due to the photooxidation process. Moreover, the photo oxidation was further confirmed by the presence of the new band appearing at 3536 $cm^{-1}$ accompanied by the decrease of relative intensity of absorption band at 1642 $cm^{-1}$ suggesting the formation of amines according to e.g. photo-Fries type of mechanism in polyurethanes [46], as highlighted also by EGA-MS (Figure 5).

Concerning the C-H stretching region (3000-2850 $cm^{-1}$), the surface sample CU4 showed a reduction in the band at 2970 $cm^{-1}$ (C-$H_3$ asymmetric stretching) and a relatively higher intensity of the C-$H_2$ stretching absorption at 2918 $cm^{-1}$, in comparison to CU3. These alterations could be related to reticulation processes which may occur as a consequence of the formation of reactive compounds as products of the photo-oxidative degradation of polyether-based polyurethane.

The carbonyl region (1800-1630 $cm^{-1}$) is also significant in the evaluation of foam degradation: CU4 spectrum showed the presence of bands, which were not present in the CU3 spectrum, at 1713, 1689 and 1675 $cm^{-1}$ which were identified as urethane loosely associated through H-bonds, free urea, and disordered H-bond monodentate urea respectively [38,39]. The formation of free urea is the sign of the cleavage of urethane bonds, while the bands at 1713 and 1675 $cm^{-1}$ could be related to the bond rearrangement due to cross-linking involving reaction of amines with urethane groups. In the spectrum of sample CU4, the relatively higher intensity of the band at 1015 $cm^{-1}$, corresponding to C-O stretching vibration of alcohol, indicates that hydrolysis had occurred [42]. However, the spectroscopic results highlight the persistence of a significant portion of free amines (band at 3536 $cm^{-1}$).

**Table 2** Vibrational band assignment for the ATR-FTIR spectrum of sample CU3 (bulk) from "Contenitoreumano n.1", shown in Figure 3.1 [19,38-42].

| Wavenumber ($cm^{-1}$) | Assignment |
|---|---|
| 3661 - 3434 | ν N-H (non H-bonded) |
| 3293 | ν N-H (H-bonded) |
| 3016 - 3112 | ν C-H (benzene ring) |
| 2971 | $\nu_a$ C-$H_3$ |
| 2929 | $\nu_a$ C-$H_2$ |
| 2895 | ν C-H |
| 2868 | $\nu_s$ C-$H_3$ |
| 1726 | ν O=C (urethane, non H-bonded) |
| 1642 | ν O=C (bidentate urea, ordered H-bonded) |
| 1599 | ν C=C (benzene ring) |
| 1538, 1262 | δ O=C-N-H ν O=C-N-H |
| 1474 | δ C-$H_2$ |
| 1451 | $\delta_a$ C-$H_3$ |
| 1412 | Trimer band (isocyanurate ring) |
| 1373 | $\delta_s$ C-$H_3$ |
| 1343 | ω C-$H_2$ |
| 1296, 1225 | ν C-N |
| 1095 | $\nu_s$ C-O-C (polyether-based polyol) |
| 1015 | ν C-O-H |
| 927 | ρ C-$H_3$ |
| 868, 817, 770 | ω C-H (benzene ring) |
| 710, 673 | δ C-H (benzene ring) |

**Table 3** Vibrational band assignment for the ATR-FTIR spectrum of sample CU4 (surface) from "Contenitoreumano n.1", shown in Figure 3.2 [19,38-42]

| Wavenumber ($cm^{-1}$) | Assignment |
|---|---|
| 3536 | ν N-H (non H-bonded) |
| 3408 - 3376 | ν O-H (H-bonded) |
| 3293 | ν N-H (H-bonded) |
| 3121 - 3005 | ν C-H (benzene ring) |
| 2970 | $\nu_a$ C-$H_3$ |
| 2918 | $\nu_a$ C-$H_2$ |
| 2897 | ν C-H |
| 2871 | $\nu_s$ C-$H_3$ |
| 2865, 2852 | $\nu_s$ C-$H_2$ |
| 1723 | ν O=C (urethane, non H-bonded) |
| 1713 | ν O=C (urethane, loosely associated through H-bonds) |
| 1689 | ν O=C (urea free) |
| 1675 | ν O=C (monodentate urea, disordered H-bonded) |
| 1643 | ν O=C (bidentate urea, ordered H-bonded) |
| 1600 | ν C=C (benzene ring) |
| 1538, 1262 | δ O=C-N-H ν O=C-N-H |
| 1472, 1464 | δ C-$H_2$ |
| 1452 | $\delta_a$ C-$H_3$ |
| 1416 | Trimer formation band (isocyanurate ring) |
| 1373 | ω C-$H_2$ |

| | |
|---|---|
| 1344 | $\delta_s$ C-$H_3$ |
| 1297, 1225 | ν C-N |
| 1096 | $\nu_a$ C-O-C (polyether-based polyol) |
| 1017 | ν C-O-H |
| 927 | ρ C-$H_3$ |
| 870, 817 | ω C-H (benzene ring) |
| 758, 710, 668 | δ C-H (benzene ring) |

### 3.3 EGA-MS

Figure 4 shows the overlaid EGA-MS curves of the two samples from "Contenitoreumano n.1". EGA-MS provides thermal degradation profiles and chemical information on the thermal decomposition products of PUs through their mass spectra [47].

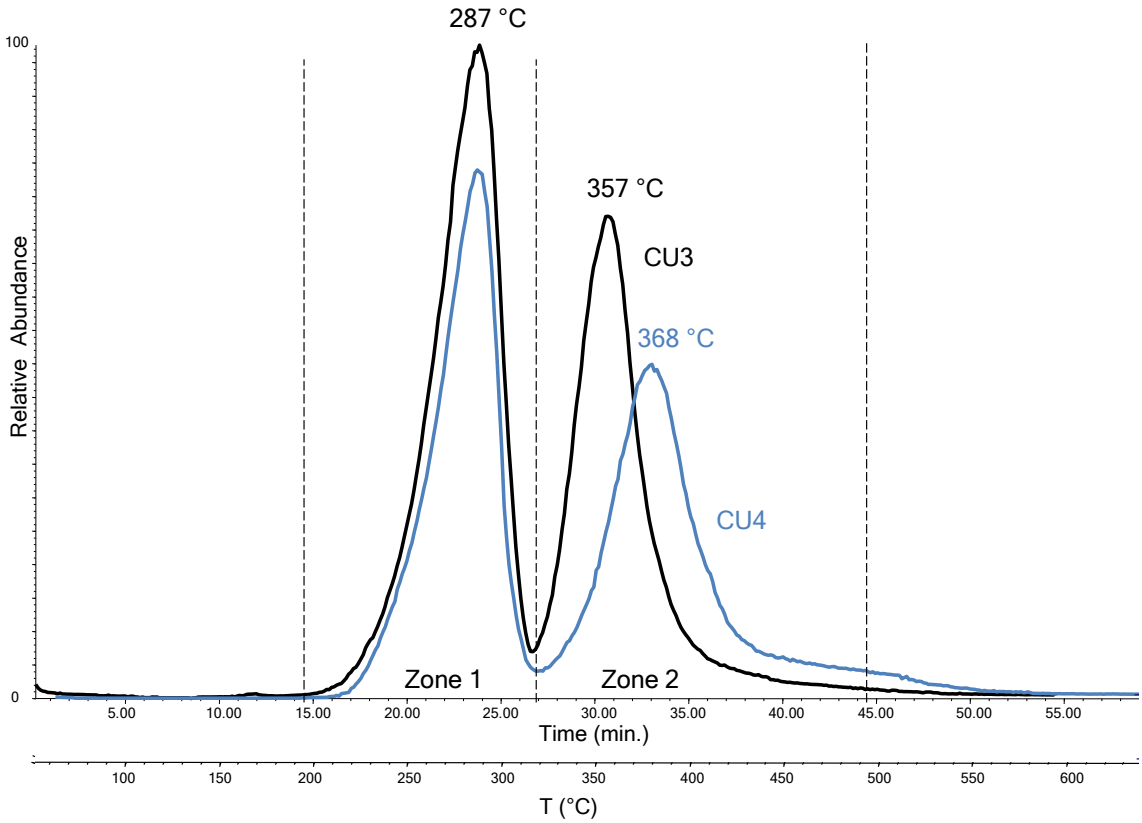



**Figure 4** EGA-MS curves obtained for the bulk sample CU3 (black curve) and surface sample CU4 (blue curve) from "Contenitoreumano n.1". The curve intensity was normalised for the weight of the samples.

Two thermal decomposition zones were detected for the "Contenitoreumano n.1" PU foam: zone 1 from 200 °C to 320 °C with a peak at 287 °C and zone 2 from 320 °C to 500 °C with a peak at 357 °C for sample CU3, and a peak at 368 °C for sample CU4. The first thermal degradation step is related to the desorption of additives and plasticizers and to the first step of the depolymerisation of polyurethane linkage in the temperature range 250-300 according to the literature [48], leading to isocyanate-terminated chains with diminished molar mass.

The most abundant ions in the mass spectra of this region were fragments with m/z 174, 148, 145, 132, 106, 77, 65, 51 which correspond to 2,6-toluenediisocyanate, and 149, 121, 132, 93 which correspond to phthalates [49].

The second thermal degradation step is related to the complete pyrolysis of the polymeric network. The most abundant ions in the mass spectra of the second thermal degradation zone in the mass spectra were fragments with m/z 117, 101, 87, 73, 59 attributable to the fragmentation of polyether-based polyols constituting the soft segments of PU , such as polypropylene glycol [50] of polyurethane.

Comparing the EGA profiles of the two samples, the first step thermal degradation temperature was the same for both samples, while the EGA curve of sample CU4 showed a 50 °C increase in the degradation temperature of the polymeric network. This may be caused by the cross-linking process which leads to an increase in the hardness and brittleness of the foam.

Significant ions were extracted from the EGA profiles in order to compare the bulk sample CU3 and surface sample CU4 (Figure 5).

The fragmentograms of these significant ions were compared for the two samples: ions with m/z 149 which corresponds to phthalates, m/z 148 which corresponds to a toluene diisocyanate (TDI) with one isocyanate group replaced by an amino group, and m/z 59, an oligomer of polyether-based polyol. From the extracted ion thermograms, the main difference between the two samples was a reduction in the amount and type of phthalates (m/z 149) in the surface sample (CU4). This could indicate that degradation leads to a loss in the volatile component of additives.

In particular, in the degraded sample CU4 the contribution of isocyanate with one isocyanate group replaced by an amino group (ion m/z 148) was relatively higher than in CU3, when compared to the intensity of the polyols fragments (ion m/z 59).

Interpreting the EGA-MS results together with the FTIR-ATR results we can hypothesize that the photooxidation caused more pronounced changes in the soft segments of PU, leading to the volatilization of low molecular weight products, suggested by the decreased intensity of the absorption band at 1096 $cm^{-1}$ in the CU4 sample, and higher contribution of isocyanate derivatives in the volatile compounds, indicating a decreased ratio of the soft to hard segments as a result of 50 years of ageing, which has induced an higher concentration of NH substituted terminal groups in the pyrolysis products (as confirmed by the appearance of the FTIR band at 3536 cm-1 in the degraded sample CU4).

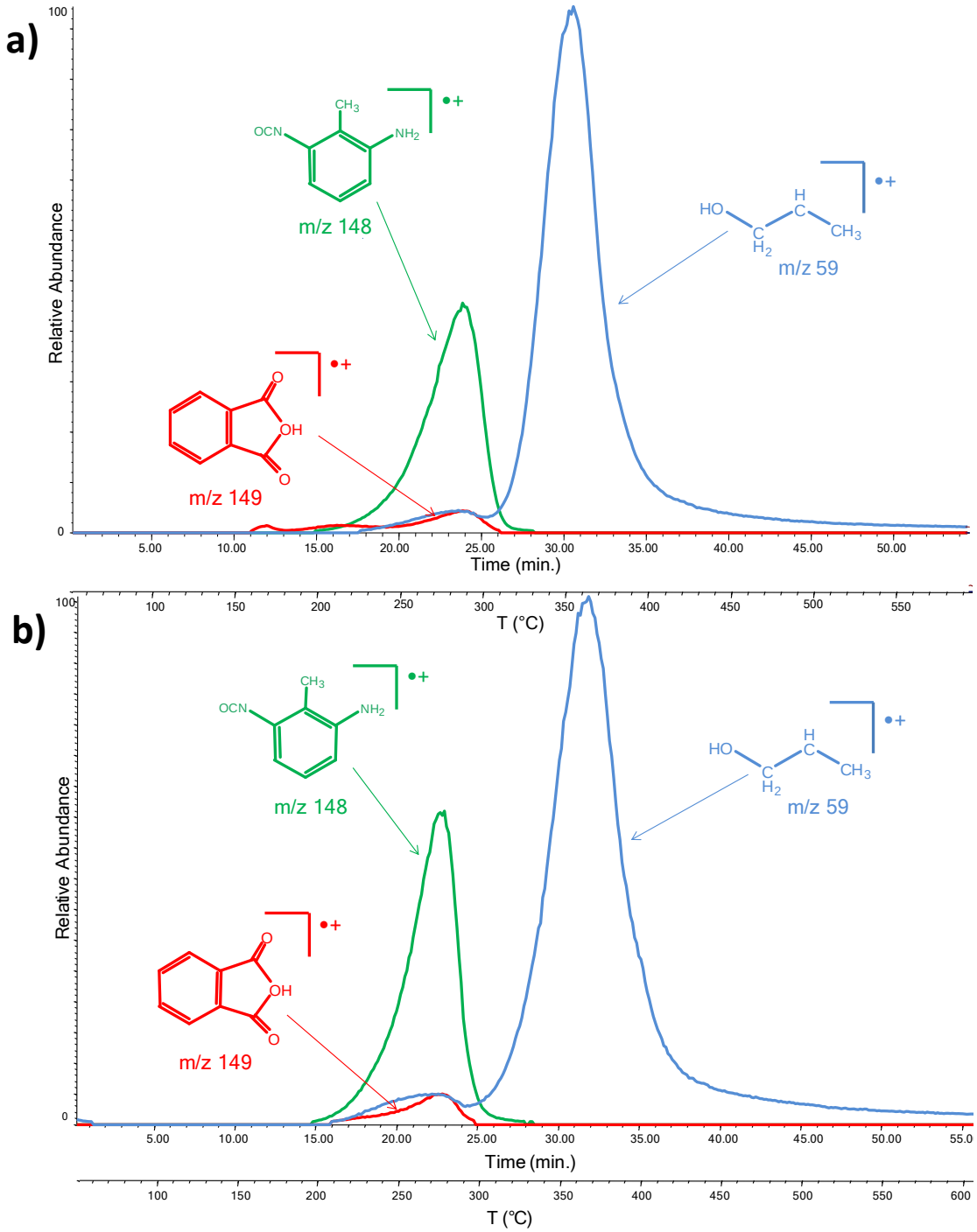



Figure 5 Extracted ion (m/z 59, 148, and 149) thermograms of evolved gas during the thermal degradation obtained for the bulk sample CU3 (a) and surface sample CU4 (b) from "Contenitoreumano n.1"

### 3.4 Py-GC/MS

Double-shot pyrolysis temperatures for the Py-GC/MS analysis of "Contenitoreumano n.1" were selected on the basis of the EGA profiles. The temperatures for the two steps (306 °C and 600 °C) were selected at the end of the EGA-MS bands (Figure 4) in order to collect all the evolved products.

Figure 6 shows first-shot pyrograms at 306°C of the bulk sample CU3 and the surface sample CU4, respectively. The peak identification is reported in Table 4.

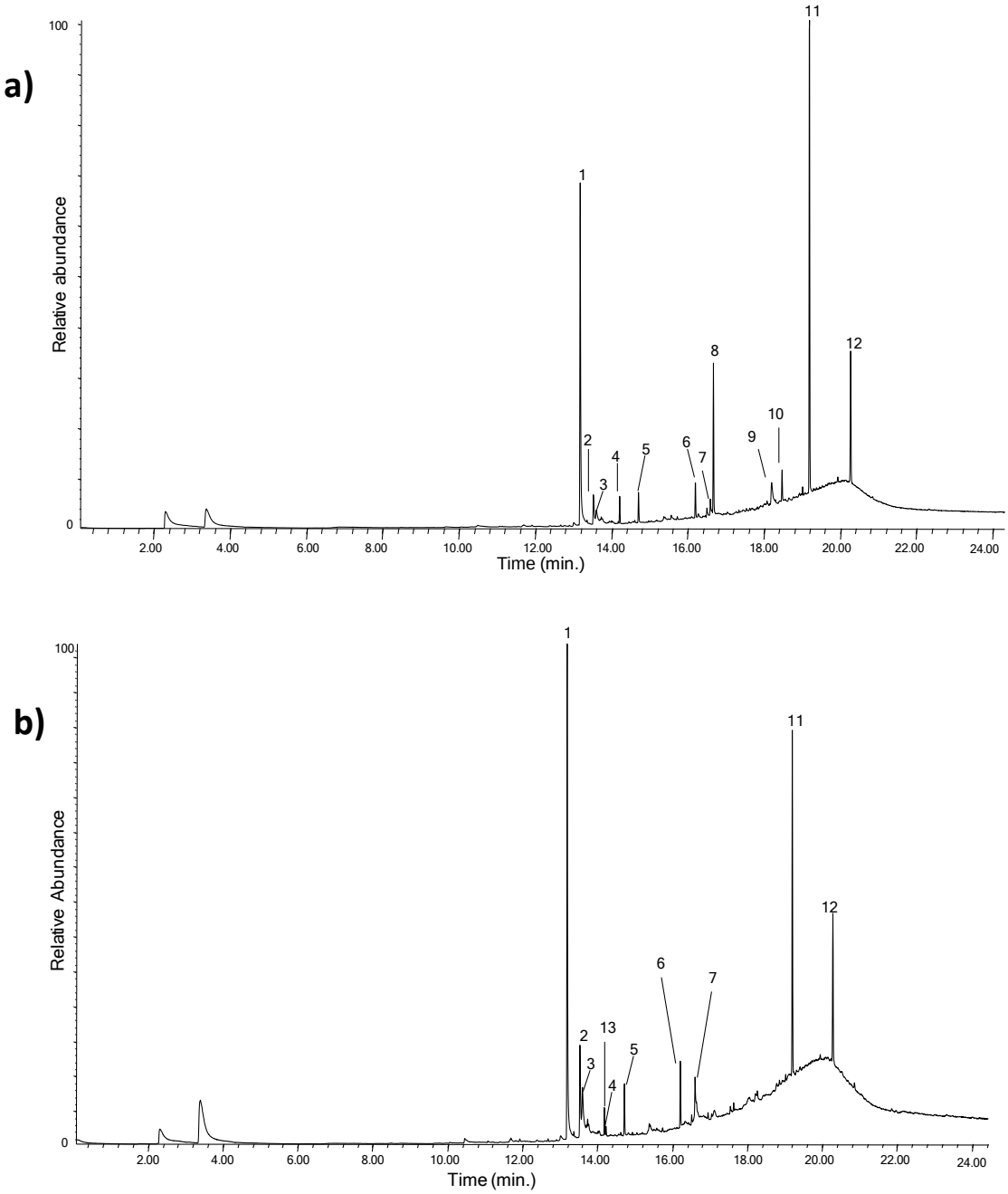



Figure 6 Py-GC/MS chromatogram obtained after first-shot pyrolysis at 306 °C of a) sample CU3 (bulk PU foam) and b) sample CU4 (surface PU foam) from "Contenitoreumano n.1". Peak identification is reported in Table 4.

In the first-shot pyrogram of both samples, the most abundant species are free 2,6-diisocyanatetoluene (n°1) [29,51] (identified as the precursor used in the synthesis of the

polyurethane foam), its rearrangement products 2-amino-6-isocyanatotoluene (n° 2,3) [28], and phthalic acid esters (n° 5, 6, 8, 10, 11).

Phthalates are the most widely used plasticizers in the synthesis of polyurethane, and account for 92% of all plasticizers[52]. The main differences highlighted from the comparison of the pyrograms of the two samples were: the change in the relative abundance of the isocyanate peak (n° 1) and the reduction in the amount and type of phthalates (loss of di-n-butyl phthalate and butyl benzyl phthalate) in the surface sample CU4. These changes are in agreement with the EGA information.

**Table 4** Identification of chromatographic peaks in the first-shot (306 °C) pyrograms of samples CU3 and CU4 from "Contenitoreumano n.1" shown in Figure 6.

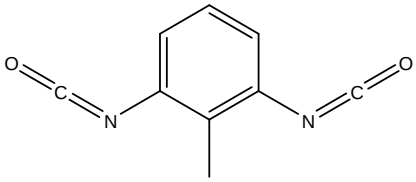
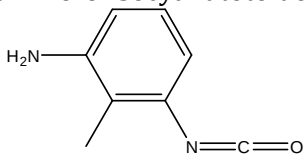
| Peak number | Peak identification | Main ions (m/z) |
|---|---|---|
| 1 | 2,6-diisocyanatotoluene  | 174,145, 132, 118, 91 |
| 2 | 2-amino-6-isocyanatotoluene  | 148, 120, 106, 93, 77, 65, 52 |
| 3 | 2-amino-6-isocyanatotoluene (*isomer*) | 148, 119, 106, 93, 77, 65,51 |
| 4 | 4-methyl-2,6-di-tert-butylphenol | 220, 205, 145, 57 |
| 5 | Diethylphthalate | 177, 149, 105, 93, 76, 65 |
| 6 | Di-isobutylphthalate | 223, 149, 104, 76, 57 |
| 7 | Hexadecanoic acid | 256, 213, 129, 115, 73, 60 |
| 8 | Di-*n*-butylphthalate | 223, 205, 149, 104, 76 |
| 9 | 2-cyclohexen-1,4-diol | 105, 96, 70 |
| 10 | Butylbenzylphthalate | 312, 238, 206, 149, 104, 91, 65 |
| 11 | Bis(2-ethylhexyl) phthalate | 279, 167, 149, 113, 93, 83, 71, 57 |
| 12 | Squalene | 410, 148, 137, 121, 109, 95, 81 |
| 13 | 2,4-di-tert-butylphenol | 206, 191, 91, 74, 57 |

Figure 7 shows second-shot pyrograms at 600 °C of the bulk sample CU3 and the surface sample CU4, respectively. The peak identification is reported in Table 5.

In the time range of 0-10 minutes, the main pyrolysis products derived from chain extenders and cross-linkers such as n-butane, diethylamine and butanamide. Between 10 and 13 minutes 2,6-

diisocyanatotoluene (n° 15) and its rearranged molecule (n° 7), and derivatives of propylic alcohol, derived from the polymeric network were observed. A cluster corresponding to different chain length ether oligomers (m/z 174, 148, 117, 101, 87, 73, 59) was observed in the time range of 13-22 minutes. The polyether-based polyol used in the synthesis of this PU foam was found to be polypropylene glycol [28] from the analysis of the mass spectra (m/z 117, 87, 73, 59).

A comparison of the pyrograms at 600 °C of the samples from "Contenitoreumano n.1" did not show significant differences between the two samples. The higher decomposition temperature observed in the EGA profile of sample CU4 was not associated with a different qualitative and quantitative profile of pyrolysis products. This is concurring with the occurrence of crosslinking.

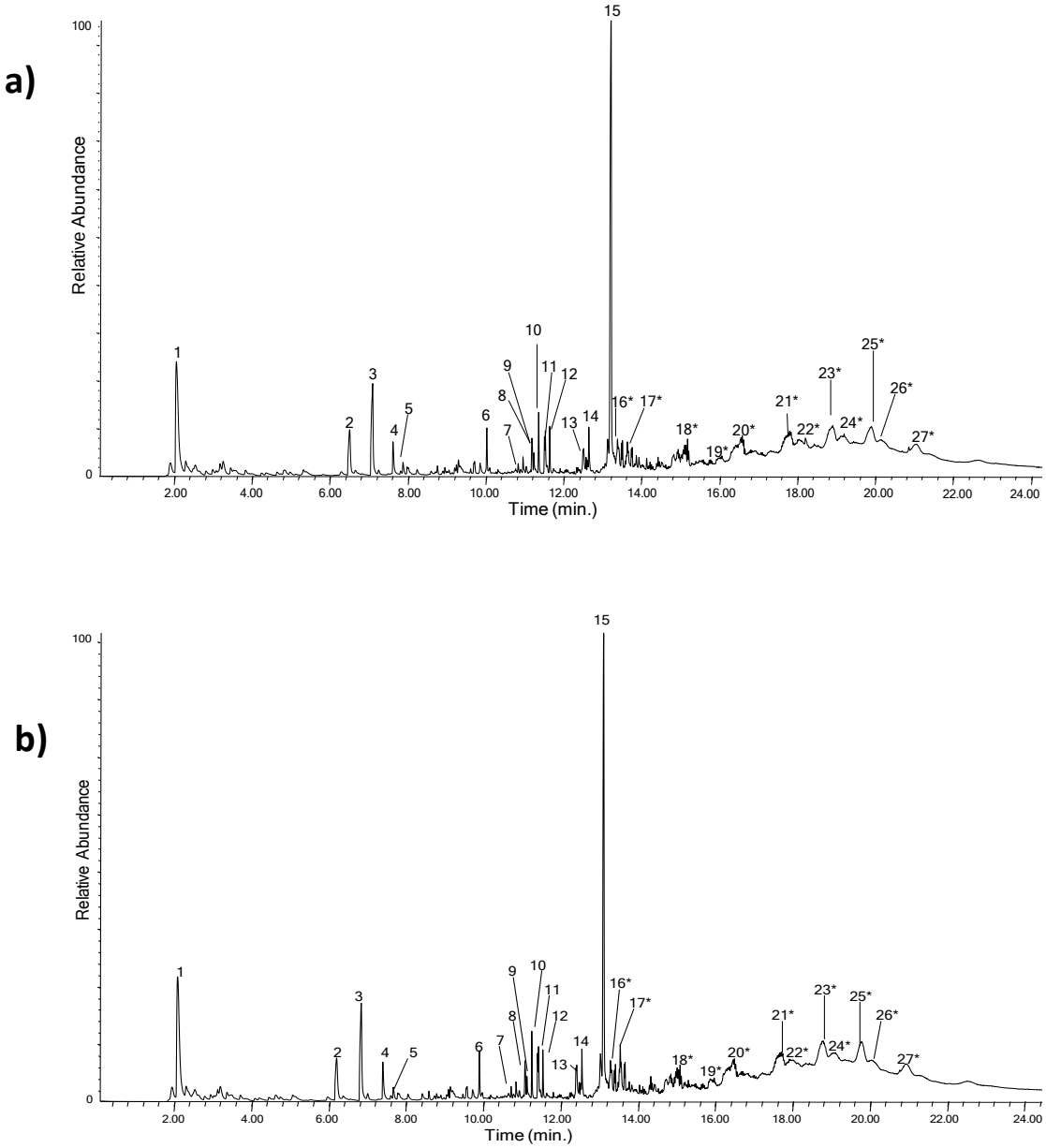
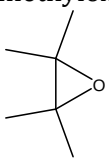
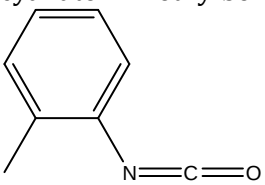
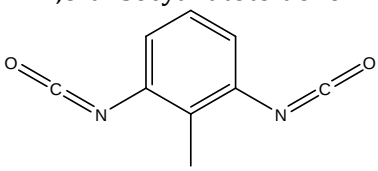
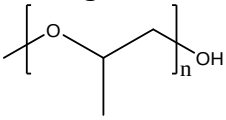
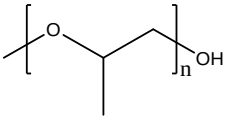
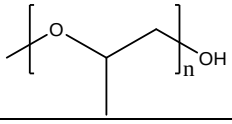



Figure 7 Py-GC/MS chromatogram obtained after second-shot pyrolysis at 600 °C of a) sample CU3 (bulk PU foam) and b) sample CU4 (surface PU foam) from "Contenitoreumano n.1". Peak identification is reported in Table 5.

**Table 5** Identification of chromatographic peaks in the second-shot (600 °C) pyrograms of samples CU3 and CU4 from "Contenitoreumano n.1" shown in Figure 7.

| Peak number | Peak identification | Main ions (m/z) |
|---|---|---|
| 1 | n-butane | 58 |
| 2 | n-ethyl acetamide | 87 |
| 3 | Diethylamine | 73, 58 |
| 4 | Propyleneoxide | 58 |
| 5 | Butanamide | 87, 72, 59 |
| 6 | Tetramethyloxirane  | 100, 59 |
| 7 | 1-isocyanate-2-methylbenzene  | 133, 104, 91, 78 |
| 8 | 3-(3-isopropoxy)propoxy-propanol | 145, 117, 103, 87, 73, 59 |
| 9 | 1-(2-allyloxy-1-methylethoxy)-2-propanol | 103, 85, 73, 59 |
| 10 | Unknown | 131, 114, 101, 89, 73, 59 |
| 11 | Propyleneglycol trimer | 117, 103, 73, 59 |
| 12 | Unknown | 114, 101, 84, 71, 57 |
| 13 | Propyleneglycol trimer | 117, 103, 87, 73, 59 |
| 14 | 1-(1-methylpropoxy)-butane | 115, 101,83, 73, 57 |
| 15 | 2,6-diisocyanatotoluene  | 174, 145, 132, 118, 103, 91 |
| 16* | Oligomers  | 117, 87, 73, 59 |
| 17-20* | Oligomers  | 148, 117, 101, 87, 72, 59 |
| 21-27* | Oligomers  | 174, 148, 115, 101, 87, 73, 59 |

* cluster from 13.3 min to 21.6 min

## 4. Conclusions

Our multi-analytical approach based on the use of infrared spectroscopy and two different analytical pyrolysis methodologies, double shot Py-GC/MS and EGA-MS, was successfully applied in the study of the polyurethane artwork "Contenitoreumano n.1" (1968). The integrated interpretation of the results obtained with the three analytical methods enabled us to obtain a detailed picture of the composition and the state of preservation of the PU material used to produce the object. The isocyanate and polyol precursors, as well as the plasticizers, used in the production of the PU foam were identified by mass spectrometry. Different aspects of the degradation processes undergone by the surface portion of the foam were also highlighted by the three techniques, on the basis of a comparison with a sample of better preserved foam from the bulk:

- ATR-FTIR analysis revealed a combination of hydrolysis, reticulation, and photo-oxidative processes;
- EGA-MS highlighted an increase in the thermal degradation temperature of the polymer due to to crosslinking;
- double shot Py-GC/MS revealed the loss of plasticizers.

The application of EGA-MS and multi-shot Py-GC/MS in investigating synthetic polymer-based plastics in artworks and design objects appears extremely promising for future heritage studies and is worth extending to a wider range of materials and objects. When compared to conventional flash-pyrolysis coupled with GC/MS, EGA-MS and multi-shot Py-GC/MS extend the pyrolysis analyses of polymers beyond a mere identification or classification. These methods could achieve selectivity in the investigation of specific fractions and provide semi-quantitative information, such as partial cross-linking and loss of plasticizers, which could be successfully exploited to compare samples in different states of preservation.

According to these analytical results, the macroscopic appearance and brittleness of the degraded portion of the PU foam could be related to parallel processes of photolysis and hydrolysis, together with a partial reticulation and cross-linking involving the hydrolyzed portion of the PU foam. In detail, photooxidation of polyether-based PUs component lead to molecular mass degradation accompanied by crosslinking that could be considered as prevailing mechanisms in soft segments ageing.

The surface in fact showed a lower elasticity than the internal part of the object. The loss of plasticizers leads to a further worsening of the physical properties, leading to fragmentation and loss of foam flakes.

On the basis of the results of the investigation performed on "Contenitoreumano n.1", the Triennale Design Museum Conservation Department decided to plan a restoration, which included a dry-cleaning protocol and gluing of the layers. Consolidation was considered but not carried out at this stage due to the fairly good condition of the bulk of the foam [31].

**Acknowledgments**

The authors would like to thank Silvana Annicchiarico, Director of the Triennale Design Museum (Milan), and Rafaela Trevisan of the Conservation Laboratory of the Museum for their essential contribution in the investigation of “Contenitoreumano n.1”. The research was funded by the IPERION-CH.it Platform as part of the ALRTDM Project “Plastic materials in the Collection of Triennale Design Museum in Milan”, and by the University of Pisa as part of the PRA_2016_13 Project "Analytical chemistry for the knowledge of materials and techniques in modern and contemporary art”. The authors also acknowledge three anonymous reviewers for useful comments and suggestions.

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