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Detection of degradation markers from polymer surfaces by a novel SERS-based strategy

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ABSTRACT

This paper provides new insights for the study of polymer degradation through the detection of markers released at the polymer surface using Al-coated SERS active substrates. Combining a nanodestructive sampling procedure with the SERS sensitivity allows achieving detection limits much lower than traditional polymer characterization techniques, opening the way to the use of SERS as part of an innovative strategy to diagnose surface degradation in polymeric museum artefacts. The method was applied to artificially photo-aged model polymers and to museum artworks.

1. Introduction

The application of Raman spectroscopy to polymers has a very long history, starting with the collection of the first spectrum of a polymer by Signer and Weiler [1], then followed by the early expansion in the 60 s' due to the advent of laser excitation [2]. Later, a renewed interest for both research and quality control applications was stimulated by the development of new efficient detectors, tuneable lasers and Fourier transform instrumentation [3]. As an example, Raman spectroscopy has been widely used to identify polymeric systems [4] and for monitoring polymerization processes [5–7], as well as for the study of degradation [8]. In addition, the other levels of hierarchical organization of structure in polymers, i.e. stereoregularity [9], chain conformation and crystallinity [10–12], may also be investigated by conventional Raman systems. Further potentials of the technique are being explored through the development of surface-enhanced Raman spectroscopy (SERS) [13], in which amplification of the signal mainly arises from the interaction of the Raman transition moment of the adsorbed molecules with the light-induced electromagnetic fields on the appropriate metal surface.

SERS enabled sophisticated studies of chain diffusion in the nanometric scale [14], while expanding the understanding of polymer-metal interface phenomena [15–17]. At the same time, the intrinsic features of this technique, suitable for trace analysis and sensing, could be used to obtain information on forming functional groups, as in specific surface reactions on polymer thin films [18,19]. Surprisingly, the study of the degradation mechanisms of polymers, limited by the sensitivity of the experimental methods, has been only marginally faced by SERS or resonance Raman spectroscopies, essentially for the investigation of very peculiar systems [16,20–22]. Molecular changes associated with polymer degradation are commonly followed in detail by size exclusion chromatography (SEC) or other molecular weight determination methods, whereas corresponding chemical changes are monitored by spectroscopic techniques often identifying only the most abundant species [23]. Accurate and quantitative detection, e.g of polymer degradation markers, has been reported so far only for some volatile organic compounds [24,25].

The aim of this work is to offer novel methodological insights to the study of polymer ageing through the detection of low molecular weight degradation products considered as markers of degradation processes by using especially developed Al-coated SERS active substrates [26,27], in combination with a nanodestructive sampling procedure. The inherent problem of polymer deterioration is especially important in modern and contemporary art, and design collections. Since the last decades, conservators and heritage scientists are focusing on the evaluation of the actual state of conservation of polymeric objects to predict their durability and establish conservation and management strategies [28,29]. In such sense, the development of analytical tools that may not only detect evidence of their degradation by a non-destructive method but also follow its evolution is of utmost importance.

The well-known process of autoxidation of hydrocarbon polymers entails the formation of novel oxygen-containing groups in the main chain through a series of primary and secondary radical reactions that

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involve chain scissions, with formation of molecular fragments in a range of molecular weights between that of the original macromolecules and those of volatile molecules, and cross-linking [30]. The detailed mechanism of oxidative degradation of a polymer is usually proposed on the basis of the detection of the groups formed during ageing, as well as taking into account molecular weight changes and the possible formation of gaseous species, often underestimating the importance of difficult-to-detect non-volatile low molecular weight products. Herewith we show that the identification of such markers allows both emphasizing the beginning of oxidation and gaining knowledge of otherwise very complex routes of degradation.

2. Experimental part

2.1. Fabrication of substrates

Substrates were fabricated by ultraviolet nanoimprint lithography (UV-NIL) using a commercial nanostructured surface (Klarite®, Renishaw diagnostics) consisting of a square lattice of inverted pyramidal pits as a master mould. Inverted replica were produced through a two-step NIL protocol where the first liquid polymer material was the two component heat-curing Sylgard 184 (Dow Corning), cured at 80 °C for two hours. The neat silicone replica was then used without further treatment as a secondary mould to fabricate the direct replica of the master mould, and filled with a drop ($< 10\,\mu L$) of a liquid UV-curable elastomeric tetraurethane acrylate perfluoropolyether derivative [26]. Glass (1 mm thick) was used as both Supporting Material and planar back surface. A mask aligner with a UV-light source based on LEDs (Midas System MDA 400LJ) was used as a radiation source (beam wavelength filtered for *i*-line = 365 nm, intensity 20 mW cm^{-2}) with a 60 s exposure time. Polymeric replicas were coated with aluminum by thermal evaporation. More details on the fabrication procedure are reported elsewhere [27]. The quality of the polymeric replicas was checked by high resolution field emission scanning microscopy (HR-FESEM Zeiss Ultra-Plus).

2.2. Preparation of polymer thin films and degradation treatments

Reference polymers in form of thin films for ageing treatments were selected among those commercially available. Reference PI is a vulcanized natural *cis*-1,4-polyisoprene for healthcare applications (Semperguard, Semperit Group), with a thickness of 40 µm. A PVAc emulsion, commercially available as Rayt white glue, was used for the preparation of self-supporting 100 µm thick films. ABS films with a thickness of 100 µm were obtained by extrusion from Magnum 3404 ABS (Dow Chemicals) pellets.

In order to investigate the weathering processes of polymers in times shorter than those necessary under natural conditions, accelerated conditions must be applied, in which the different factors affecting polymer oxidation, i.e. quality and quantity of radiation, temperature and humidity, are opportunely controlled. To provoke under simulated conditions the same chemical changes as those occurring in the long term under the permanent physicochemical stresses of the environment, we chose an easily applicable tests of accelerated ageing among those usually performed to assess polymer durability. Accelerated photodegradation was carried out in a high-speed exposure unit Suntest CPS + (Heraus), equipped with a xenon light source having a constant irradiation at a power of 765 W m^{-2}; a glass filter with cut-off at $\lambda < 295$ nm was used to exclude radiation more energetic than that of outdoor daylight exposure. The maximum temperature of the samples during irradiation was 45 °C black panel temperature.

2.3. Raman spectroscopy and other characterization techniques

Raman spectra were collected in a Spectrometer Renishaw InVia Flex, equipped with two continuous wave lasers emitting at 785 nm and 514 nm, with gratings of 1200 and 1800 lines mm^{-1}, respectively, and a Renishaw CCD 576 × 400 pix detector. All the SERS measurements were performed with a long 0.50 NA NPlan long working distance objective (Leica 566036) operating with a 65 µm slit opening, with a 10 s accumulation and 1% laser power, corresponding to 0.09 mW for the 514 nm laser and 9 mW for the 785 nm laser. Sampling from aged surfaces was carried out by 1 × 0.5 cm silicone strip samplers fabricated by casting and thermal curing of a liquid prepolymer (Silgard 184, Dow Corning) under vacuum at 80 °C for 2 h, using a nylon webbing strip as a mould.

IR absorption spectra in attenuated total reflectance (ATR) mode were collected with a Thermo Nicolet 6700 FTIR instrument equipped with a Smart Endurance device, and a mercury cadmium telluride (MCT) detector, at 4 cm^{-1} resolution for 128 scans. Spectroscopic acquisition and data treatment were performed using Omnic version 7 (Thermo Nicolet). SEC analysis was performed at 40 °C in a PL-GPC 50 Integrated GPC/SEC System (Agilent) with a PL gel 3 µm MIXED-C (0.200–200 kDa) column calibrated against polystyrene standards and a differential refractometer as a detector, operating with THF as eluent (1.0 mL min^{-1}). Conventional Py-GC/MS was performed with a Pyroprobe 5000 (CDS Analytical) coupled to a 6890 N GC and 5975 B MSD (Agilent Technologies). Samples were embedded in glass wool-containing fire-polished quartz tubes and pyrolyzed at 650 °C for 10 s (heating rate 10 °C ms^{-1}). The pyrolysis-GC interface, GC inlet, and GC/MS interface were set at 325 °C. The GC was equipped with a (non-polar) HP-5MS 5% phenyl, 95% dimethylpolysiloxane column (length 30 m; internal diameter 0.25 mm; film thickness 0.25 µm). Helium was used as a carrier gas (constant gas flow, 1 mL min^{-1}). The GC oven was heated from 50° to 325 °C at 20 °C min^{-1}. The ion source of the MS operated in electron impact mode (70 eV) at 230 °C and the quadrupole detector was held at 150 °C, measuring fragments in the *m/z* 50–500 range.

3. Results and discussion

A series of reference industrial polymers considered as representative of different degradative behaviours of vinyl polymers were submitted to artificial photo-ageing conditions. Their changes were followed by SERS as well as traditional techniques, such as FTIR and Raman spectroscopy, SEC and pyrolysis-gas chromatography–mass spectrometry (Py-GC/MS). The selection of acrylonitrile-butadiene-styrene copolymer (ABS), poly(vinyl acetate) (PVAc) and polyisoprene (PI) was also done on the basis of their aesthetic rendering and mechanical properties, which make them materials of choice for the realization of rapid prototyping in art [31], flexible design objects [32] and soft-touch artworks [29], respectively. In particular, aged thin films were sampled by using silicone strip samplers gently pressed onto the exposed surface for 10 s. Physisorbed molecules were then dissolved in around 10 µL of an adequate solvent, usually THF, and transferred onto SERS-active Al-coated 3D structures (the three-step procedure is schematized in Fig. 1, where representative images of the SERS substrate are also shown). The substrates have an average SERS enhancement factor of around 10^9 for a 514 nm excitation wavelength, as determined for rhodamine 6 G [27].

The upper molecular weight limit of the molecules extracted by the silicone strip sampler has been evaluated against blends of polymers with precise molecular weights and narrow distributions, i.e. polystyrene and poly(ethylene glycol) SEC standards, being around 2.1 kDa for apolar and 1.5 kDa for polar molecules. The average lower molecular weight cutoff is approximately 500 Da. ABS is a common thermoplastic, consisting of styrene-acrylonitrile segments grafted onto polybutadiene chains. Its oxidation primarily occurs in the polybutadiene fraction yielding oxygenated species such as hydroperoxides, ketones and esters through a typical auto-oxidation mechanism [33,34]. Photo-oxidation products detectable with our sampling procedure are already visible after some tens of hours of accelerated

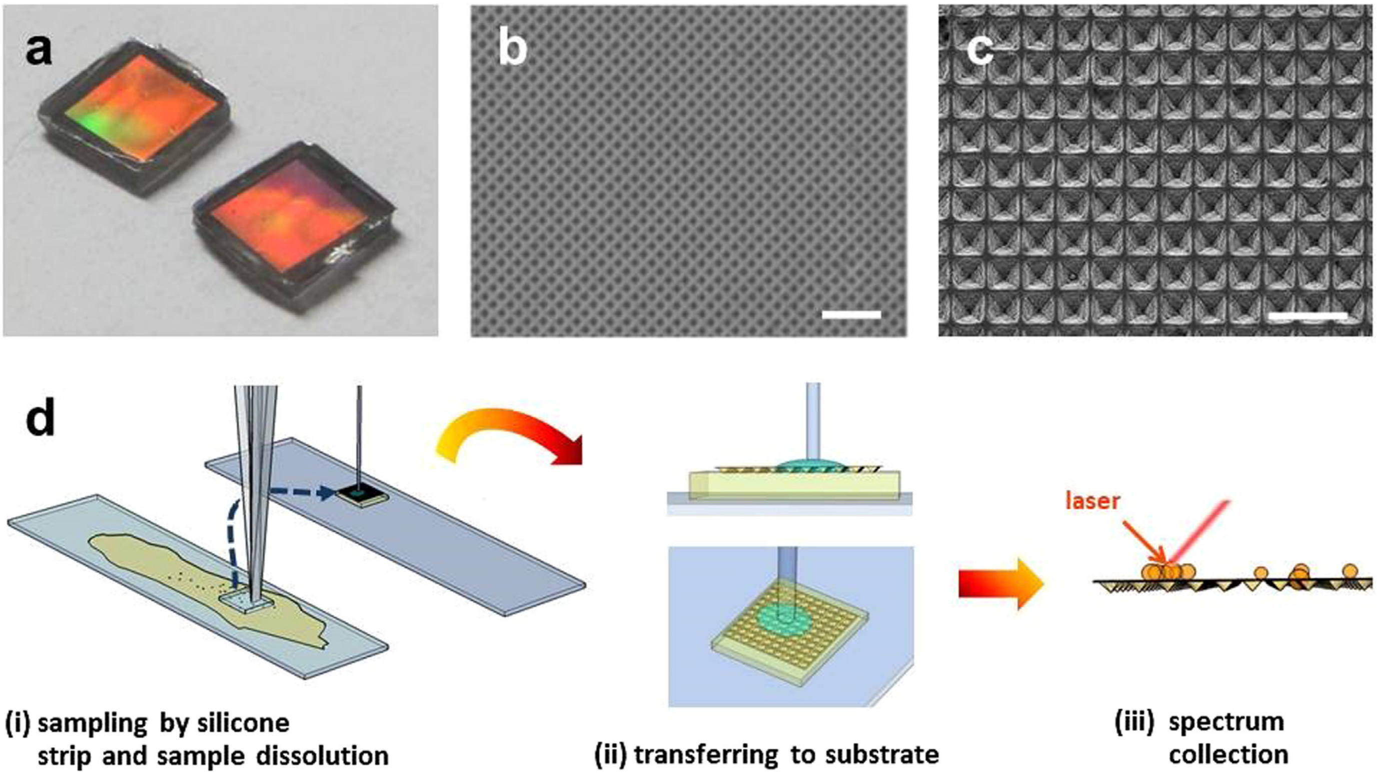

Fig. 1. Photograph of 5 × 5 mm Al-coated 3D SERS substrates (a); SEM micrographs with different magnification of the inverted pyramidal surface of the substrate (b, scale bar 10 µm; c, scale bar 5 µm) and cartoon schematizing the 3 step sampling procedure (d). Photographs corresponding to the different steps are shown in the Supplementary Information, Fig. S1.

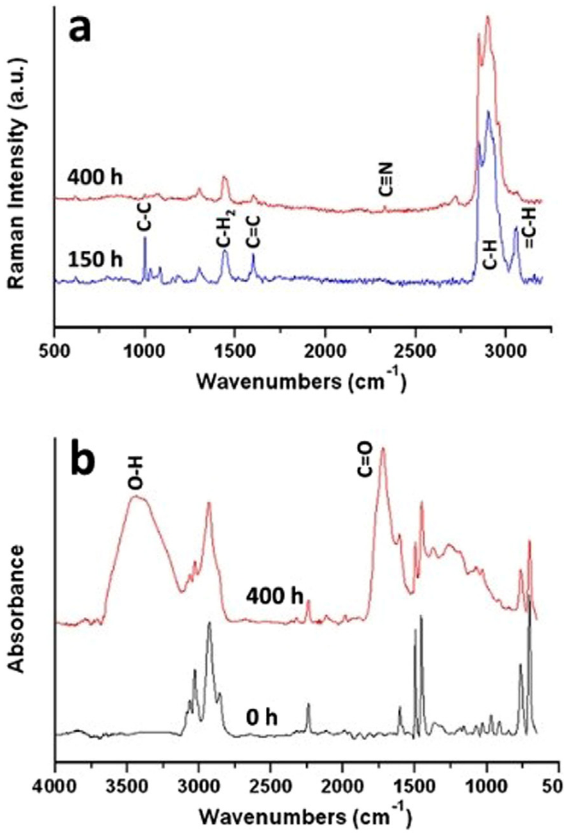

Fig. 2. SERS spectra at 514 nm excitation wavelength of surface products from 150 and 400 h photo-aged ABS (a); and ATR-FTIR spectra of pristine ABS, compared with that of 400 h photo-aged ABS (b).

ageing, in conditions in which the formation of low molecular weight products cannot be detected by SEC. As a matter of fact, the initial average molecular weight, i.e. M_n = 70 kDa, decreases down to around 40 kDa after 500 h of photo-ageing, with an increase of the polydispersity index from 3.4 to 7.5, revealing the simultaneous development of limited cross-linking and chain-scission processes. Although FTIR spectra (examples in Fig. 2b) reveal an oxidation of ABS with carbonyl and hydroxyl formation, SERS spectra of products sampled from the surface, shown in Fig. 2a, indicates the presence of a negligible amount of carbonyl groups. Interestingly, shorter oxidation times induce the formation of fragments essentially consisting of polybutadiene chains [typical absorptions at 3050 cm^{-1} (ν = C-H), 2920 and 2850 cm^{-1} (ν CH$_2$), 1650 cm^{-1} (ν C=C), 1440 cm^{-1} (δ CH$_2$), and 994 cm^{-1} (ν C-C)]. In a second phase, e.g. for 400 h ageing, the spectrum indicates a decrease of unsaturation content and shows peaks due to other components, in particular at around 2300 cm^{-1} (ν CN), revealing the presence of small amounts of acrylonitrile residues. The mostly polybutadienic nature of physisorbed fragments was also confirmed by Py-GC/MS, although for this complementary analysis it was necessary to collect them from a 10 fold larger surface by repeated silicone strip sampling.

In the case of the second reference polymer, i.e. PVAc, even though its well-known mechanism of oxidation do not entail the extensive formation of oligomeric fragments [35,36], surprisingly the selectivity of the applied procedure shows the release of first degradation markers after around 100 h photo-ageing. SERS spectrum of products sampled from the surface of oxidized PVAc thin films is shown in Fig. S2, as an example. The very high sensitivity of the third polymer, PI, to oxidation results from the presence of carbon-carbon double bonds within the isoprene backbone. Limited chain-scissions and different oxidized species are produced during ageing [37,38], thus making PI an excellent testing ground to evaluate the capability of the method (for clarity the mechanism of PI oxidation is shown in Fig. S3). Surface degradation markers from artificially photo-oxidized PI were easily detectable since the beginning of ageing, and are showing the characteristics visible in the typical SERS spectrum of Fig. 3a. By comparison with the Raman spectrum of the photo-aged polymer (Fig. 3b), the same structural features are visible in both cases, although with the presence of a band at 1738 cm^{-1} in the fraction sampled from the surface after 120 h photo-ageing, and tentatively assigned to ester groups. This enrichment in carbonyls, whose signals are intrinsically very weak in Raman, suggests a process of fragmentation in which oxidized chains are preferentially released from the cross-linked network. It is worth citing that the higher surface enhancement of some Raman signals, specifically of those due to stretching vibration of CH bonds in the 2800–3000 cm^{-1} range, is inherent to the technique and may attributed to favourable orientation of the bonds onto the plasmonic substrate surface [39].

Application of the same method to contemporary artworks from the Galician Centre of Contemporary Art of Santiago de Compostela, realized in natural PI in 1996 (Fig. S4) [29], revealed the clear presence of markers of degradation. SERS spectra of surface products sampled either from the artworks (example in the upper part of Fig. 4a) or the corresponding material remainders available in the artist's studio, demonstrates the formation of small molecules essentially consisting in isoprene oligomers. Chemical changes in both reference and artistic PI were simultaneously followed by ATR-FTIR (Fig. S5), while the extended breakdown of the initially insoluble 3D network was supported by SEC measurements (Fig. 4b). The last ones show the formation of increasing amounts of soluble molecules having average molecular weights inversely proportional to ageing time. The 20% by weight of soluble PI chains with $M_n = 135$ kDa released after 120 h artificial photo-ageing, increases up to around 50% of the initial network after 22 years natural ageing, with M_n decreasing to 27 kDa.

Based on these evidences, the relevance of this approach is threefold:

1. From a general point of view, the proposed procedure enables for the first time to detect very small amounts of molecular fragments formed on the polymer surface. The procedure may be defined as nanodestructive, with a total amount of extracted sample in the order of 10^{-10} g.[2]
2. In a specific perspective, the application of 3D SERS substrates provides a novel tool for studying polymer ageing through a direct identification of oligomeric degradation markers, even in conditions in which traditional spectroscopic techniques or Py-GC/MS have not enough sensitivity. As a fact, no FTIR or normal Raman signals, neither significant pyrograms could be obtained from the samples collected by using a single silicone strip. With respect to the polymeric systems selected as behavioural models: (a) SERS analysis confirmed the well-known phenomena of chain scission of PI [37] and, in addition, revealed the specific chemical nature of fragments. Bond breaking reactions favour the release of low molecular weight molecules with high oxygen-content at the beginning of degradation; longer natural ageing times lead to the formation of isoprene oligomers, through a mechanism that worth being further studied, though beyond the scope of this communication. (b) Also the analysis of artificially oxidized PVAc offers new insights on its mechanism of degradation. Although this polymer has a good stability to oxidation and suffers from limited cross-linking and acetic acid release [35] degradation fragments after just 100 h photo-ageing were easily detected. Spectral analysis revealed an oligomeric structure with some unsaturations, possibly formed through a secondary mechanism of oxidation, little known so far. (c) The detection of polybutadiene fragments at the beginning of ABS oxidation, albeit never observed before, is in good agreement with the established mechanisms where degradation starts in the allylic positions of the polybutadiene chains [34]. The appearance of different repeating units in the extracted chains for longer ageing time may be justified through an involvement of the styrene-acrylonitrile residues in the oxidation process. A more detailed mechanism will be the subject of forthcoming investigations.
3. A relevant application of the method is the diagnosis of plastic artefacts deterioration. Detection of molecular markers at the surface states the beginning of an oxidation process, whereas their chemical identification provides details on the degradation pathways.

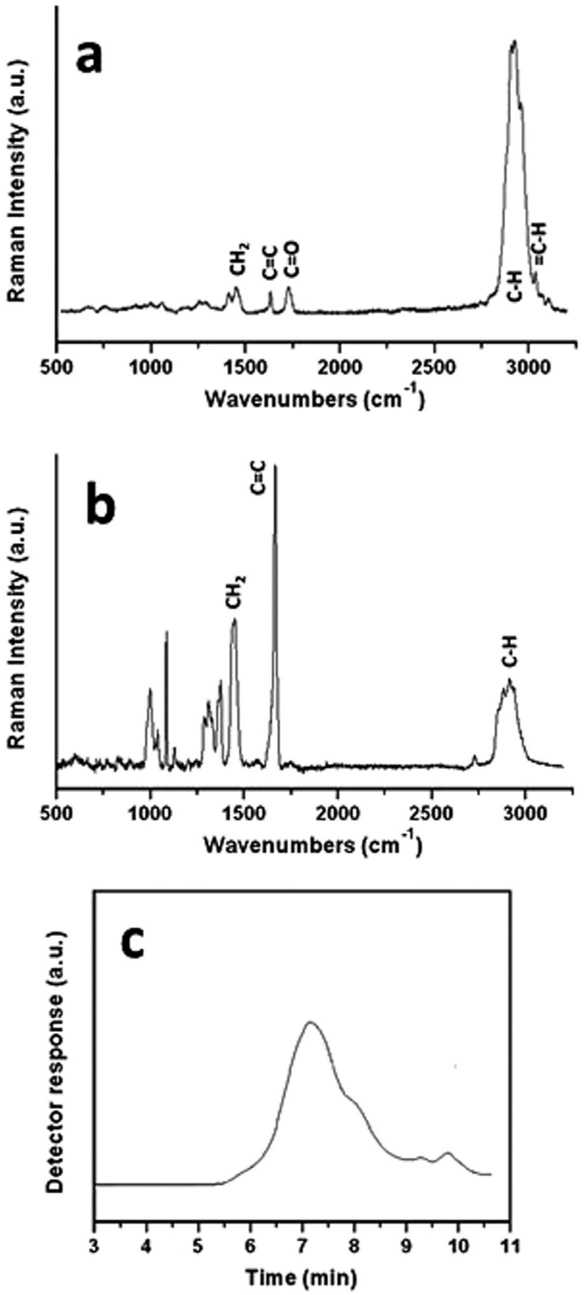

Fig. 3. SERS spectra at 514 nm excitation wavelength of surface products from 120 h artificially photo-aged PI (a), compared with the normal Raman spectrum at 785 nm excitation of 120 h artificially photo-aged PI (b); normalized SEC curve of 120 h artificially photo-aged PI (c).

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[2] The approximate amount of sample which may be extracted from the polymeric surface has been estimated from standard analytes, i.e. rhodamine 6 G and coumarin, comparing the intensity of SERS spectra obtained from due amounts of solutions with controlled concentration with those obtained from reference surfaces by silicon strip sampling.

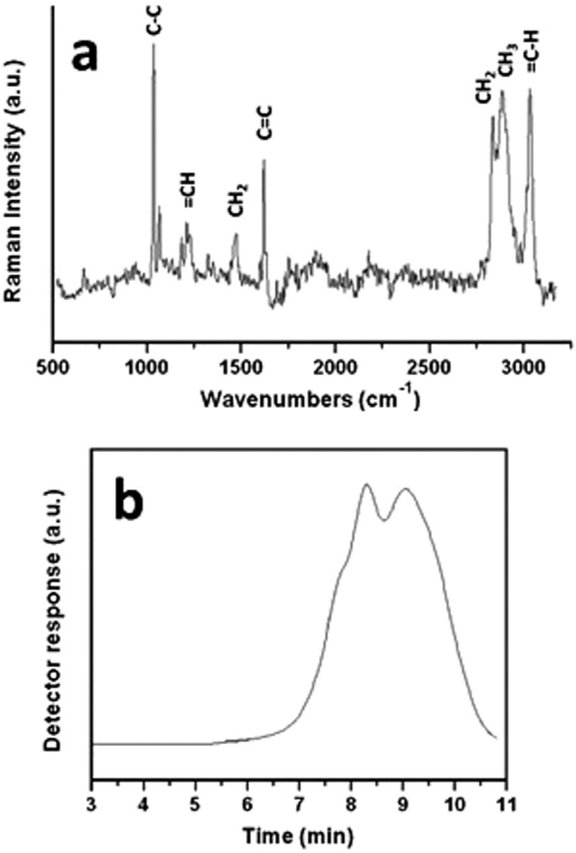

Fig. 4. SERS spectra at 514 nm excitation wavelength of surface products from 22 years naturally aged PI (a), and corresponding normalized SEC curve (b).

4. Conclusions

In summary, this proof of concept confirms the applicability of Al-coated SERS substrates in combination with a nanodestructive sampling technique for the detection of degradation markers released at the surface of polymeric materials. The sensitivity of the approach is demonstrated by analyzing oligomeric fragments resulting from the artificial photo-ageing of model polymers, namely ABS, PVAc and PI, and the natural ageing of PI museum artefacts. The procedure provides experimental evidence not achievable otherwise, and offers invaluable information on the mechanism of degradation of polymers. Finally, this enormous potential is being further explored to lower the detection limits of the procedure and to expand the knowledge on the deterioration of organic materials in artworks and museum objects [40].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2018.08.046.

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