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ORIGINAL PAPER

Analysis and aging of unsaturated polyester resins in contemporary art installations by NMR spectroscopy

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Abstract Two original art installations constructed from unsaturated polyester resins (UPR) and four different reference UPR products (before and after UVB aging) were analyzed by high-resolution 1D and 2D nuclear magnetic resonance (NMR) spectroscopy. Breaking strain studies were also conducted for the four UPR model products before and after different aging procedures (moisture, UVB exposure, melt/freeze). NMR analysis of the chemical composition of the UPR resin extracts showed they contain several low MW organic compounds and oligomers rich in polar –OH groups that play a significant role in the degradation behavior of the composite UPR materials. Statistical analysis of the NMR compositional data showed that styrene and benzaldehyde contents can be used to differentiate between fresh and aged UPR samples. The phthalate and propylene glycol unit speciation (esterified, primary or secondary –OH) of the extracts provided evidence that UPR resin C was used in the construction of the two art installations, and direct comparison of ^{1}H and ^{13}C NMR spectra verified this compositional similarity. UPR resin C was shown by both NMR and breaking strain studies to be the reference UPR most susceptible to degradation by different aging procedures, a characteristic attributed to the lower styrene content of resin C.

Keywords NMR spectroscopy · Unsaturated polyester resins (UPR) · Art installations · Organics analysis · Polymer characterization · Aging

Introduction

Polymers have become increasingly important in art collections, because, since the earliest production of polymer composite materials, artists have explored their use as sculpturing materials [1, 2]. Unsaturated polyester resins, UPR, are formed from the reaction of polyhydric alcohols with dibasic acids or anhydrides, and then subsequently dissolved and crosslinked in an unsaturated monomer, usually styrene, to produce a rigid three-dimensional polymer network, that has important applications in glass fiber-reinforced plastics [3, 4].

UPR have been used as contemporary art materials within the last 20–30 years [5, 6], because they represent inexpensive, easy to use materials and form rigid but light-weight structures. In artworks, it has been popular to use an unsaturated polyester resin to create a strong three-dimensional shape of fiberglass-reinforced polyester. However the aging of synthetic composite resin materials is known to occur faster compared to more traditional "craft" materials, such as stone and ceramics [7, 8]. Museum objects made of polymers can sometimes degrade very rapidly, and may have a useful lifetime of only a few decades [7–9]. The chemical composition and manufacturing process of polymers play a major role in shaping degradation behavior, thus analytical techniques that can identify polymer materials and study the effect of degradation on their chemical and physical properties are needed. Gas

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chromatography–mass spectrometry (GC-MS), pyrolysis-GC-MS and infrared (IR) spectroscopy have been used with success for the identification of polymeric cultural materials [7, 8], the analysis of polymeric synthetic paints [10], the study of degradation of glass-reinforced UPR [11] and the analysis of polymers used for the conservation of outdoor stone monuments [12] and frescoes [13]. NMR spectroscopy is a well-known tool for the study of synthetic macromolecules and polymer composites [14, 15]. In a cultural heritage polymers context, NMR has been used relatively scarcely so far, examples including the characterization of natural rubber artifacts, lacquers, and amber [16], the identification of polymeric paint binders [17], and the analysis of alkyds and UP resins used in commercial paint and coatings formulations [18, 19]. In the present report, we use high-resolution 1D and 2D NMR spectroscopy, in combination with dynamic mechanical studies, in an effort to highlight the effect of aging on the chemical and physical properties of UPR commercial formulations, and elucidate the effect of natural aging on two contemporary art installations constructed by UPR. The two installations, "The Last Milk Platform" (1992) by Jan-Erik Andersson and "Cocotte with Two Dogs" (1987) by Kari Tykkylainen, belong to the Oulu City Art Museum. Preliminary studies showed that there are differences in the stability and aging properties of different commercial UP products [20]. Damages, yellowing, degradation, and photo-oxidation were verified by VIS stereomicroscope investigations, CIE L*a*b* color measurements and FTIR analyses [20]. VIS microscope studies showed that UP resins and their fiberglass composites are very porous materials, which allow increased physical and chemical degradation. IR spectroscopy indicated some variations in the chemical composition of both UPR products and samples from artifacts [20].

Our approach is based on the high-resolution NMR spectroscopic study of the acetone-soluble extracts of UPR samples. We use a simple analytical protocol that contains no chemical workup, and utilizes sonication in a deuterated NMR solvent for the direct extraction of organic molecules, oligomers and polymeric material from samples obtained from works of art or the UPR reference formulations. The composition of the solvent-extractable fraction is directly determined by high-resolution NMR spectroscopy, and is used to provide insight into the extent of degradation processes that affect the physical properties during aging of the works of art. A systematic study of several model unsaturated polyester resins, prepared in the laboratory according to recipes provided by the artists that created the original works of art, and then subsequently cured and aged under controlled conditions, precedes the study of the actual works of art, in order to afford a better understanding of the UPR aging procedure. Gradient 2D NMR spectroscopy was used to assign the peaks observed in the ^{1}H and ^{13}C 1D NMR spectra of the acetone extracts. Furthermore, breaking strain measurements were conducted on all model UPR formulations after a variety of aging treatments, in order to assess the effect of aging on the mechanical properties of these materials.

Experimental section

Samples Two original art installations housed at the Oulu City Art Museum were sampled: "The Last Milk Platform" (1992) by Jan-Erik Andersson (TLMP, Fig. 1a) and "Cocotte with Two Dogs" (1987) by Kari Tykkylainen (CTD). A detailed description of the art installations can be found in Ref. [20]. The TLMP sample originated from an area of the red "mermaid" structure that was previously shown to be porous and had developed significant cracking (see Fig. 5 in Ref. [20]). The CTD sample originated from the dogs part of the installation, an area that developed significant yellowing, as depicted in Fig. 1b. Four UP resin formulations that were known to have been used by artists in Finland for the construction of art installations were studied: Synolite by Bang & Bonsomer (A); Norpol 540–800 (B); Norpol 450–500 (C); and Norpol 720–700 by Terpol Oy:s (D). The UPR reference samples were prepared in the laboratory, in accordance to the actual procedures followed by and provided by the artists in interviews (see Ref. [20] for further details).

NMR spectroscopy Deuterated acetone-d_6 was obtained from Aldrich Chemical Co., Inc. For all samples studied in this report, a small piece (3–5 mg) of the resin was dissolved in 0.6 mL of acetone-d_6 and extracted for 1 h in an ultrasonic bath. The solution was then filtered through glass wool directly into a 5-mm NMR tube.

^{1}H and ^{13}C 1D NMR spectra were obtained on either a Bruker MSL-300 or a Bruker AMX-500 spectrometer using standard instrument software and pulse sequences [21], at a probe temperature of 299 K. For the ^{13}C NMR spectra, a line-broadening of 1 Hz and drift correction were applied prior to Fourier transformation. Polynomial fourth-order baseline correction was performed before manual integration of all NMR spectra using WINNMR or TopSpin 3.0 software by Bruker. Chemical shifts in acetone-d_6 are reported relative to internal tetramethylsilane (TMS), whose proton peak was used to scale the spectrum integrals by assigning to it an integral of 1,000. ^{1}H–^{1}H homonuclear gradient COSY 2D NMR spectra [18, 21] were obtained using 256 increments of 1 K data points, 128 scans and four dummy scans with a recycle delay of 1 s. ^{1}H–^{13}C heteronuclear gradient multiple quantum correlation (gHMQC) and multiple bond correlation (gHMBC) 2D

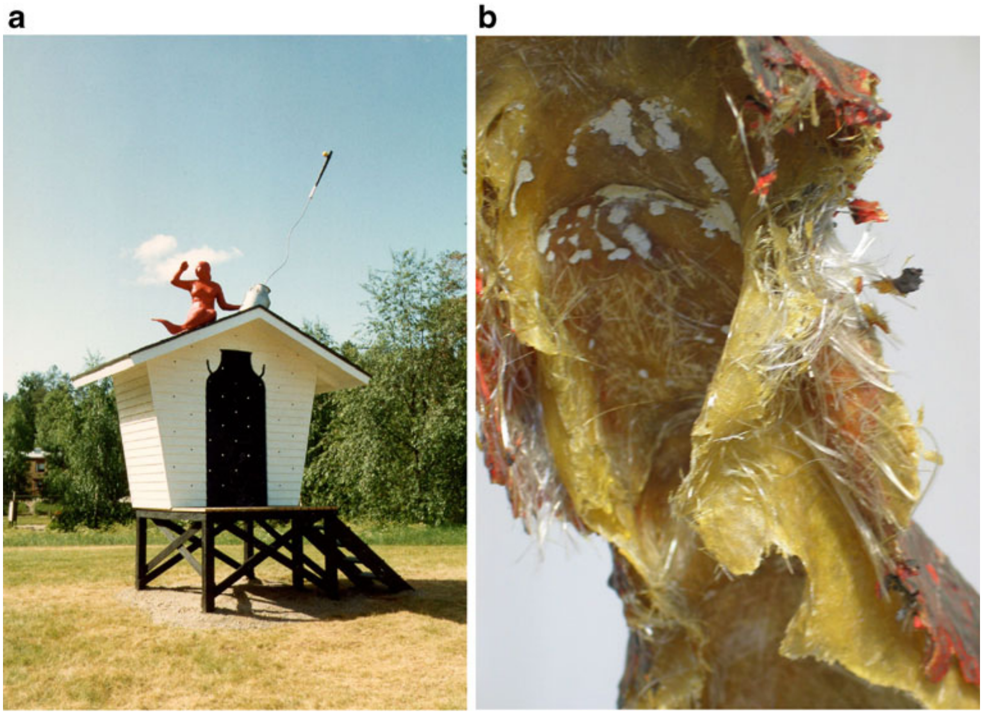


Fig. 1 **a** The installation: "The Last Milk Platform", 1992 by Jan-Erik Andersson. Reproduced with permission from Ref. [20], Fig. 2. **b** The *yellowed* UP composite layers from the dogs of the installation: "Cocotte with Two Dogs", 1987 by Kari Tykkylainen. Reproduced with permission from Ref. [20], Fig. 6. Photos by Päivi Kyllönen-Kunnas

NMR spectra were obtained using 128 increments of 1 K data points, 128 scans and four dummy scans with a recycle delay of 1 s. The gHMQC experiment was optimized for one-bond ^{1}H–^{13}C couplings of 140 Hz by setting the evolution delay to 3 ms. The gHMBC experiment used an evolution delay of 60 ms optimized for long range ^{1}H–^{13}C J-couplings of ~8 Hz [21]. Before Fourier transformation, all 2D data sets were zero-filled to a 1 K×1 K matrix, and a square-sinusoidal window function was used for processing.

Mechanical studies The reference UPR samples were subjected to different weathering conditions: (a) under moisture for 63 days, (b) 30 melt/freeze cycles, and (c) UVB exposure for 641 h, according to ISO 11507:2001 [22]. The breaking strain measurements of the reference UPR samples before and after the three different aging protocols were performed according to ISO 527-2:1993 [23] in triplicate, and average values are reported.

Statistical analysis Analysis of variance (ANOVA), principal components analysis (PCA), and hierarchical cluster analysis (HCA) were performed using Statistica 7.1, StatSoft Inc. One-way ANOVA was used to find the variables with the highest discriminatory power for two different groupings of the resin samples (state, cured/aged; type, A/B/C/D). The results of this analysis are reported as the Fisher *F* ratios and *p* level. The *F* ratio tests whether the between and within variances in a group are significantly different. The *p* level represents the probability that the observed variance of a parameter is statistically significant. PCA was used for parameter reduction and visualization of resin samples grouping. HCA was applied to explore similarity (or dissimilarity) among the various UPR samples. HCA used Ward's method as the amalgamation (linkage) rule, and Euclidean distances for the distance rule. Both PCA and HCA are unsupervised statistical methods.

Results and discussion

Organics speciation

The surface of UPR artifacts is exposed to weathering, and thus is continuously subject to chemical alterations by environmental factors, while at the same time serving as the interface through which volatile components and chemicals formed during aging escape the polymer matrix [24]. The ^{1}H 1D NMR spectra of acetone-d_6 extracts of two different cured (C, D) and subsequently UVB aged (C*, D*) UPR reference samples are presented in Fig. 2a. As expected, the NMR spectra reveal that extracts contain a diverse mixture of chemical species, including oligomeric UP chains that contain phthalic and diol units, initiators, plasticizers, degradation products etc. Figure 2b presents the 2D ^{1}H–^{1}H gCOSY spectrum of the aliphatic region of UVB aged UPR sample A*, that aided the identification of several types of free and esterified diol units in the solvent extracts of the resins. Through the extensive use of 2D

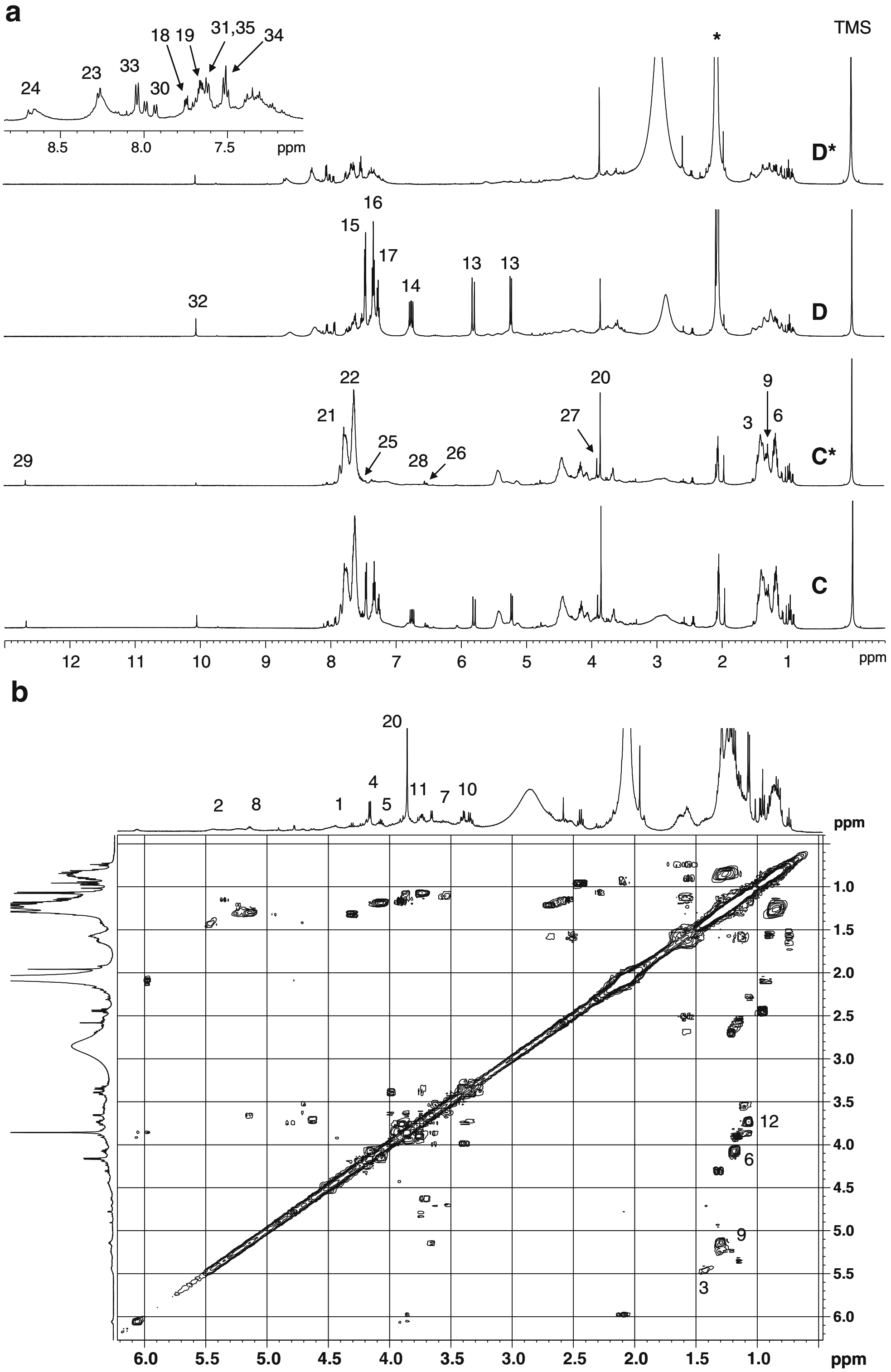


Fig. 2 **a** ^{1}H 1D NMR spectra of acetone-d_6 extracts of cured (C, D) and subsequently aged (C*, D*) standard UPR formulations, and expansion of spectrum D* **b** aliphatic region of the 2D ^{1}H-^{1}H gCOSY NMR spectrum of the acetone-d_6 extracts of aged UPR sample A*. Peak numbers refer to Fig. 3 and Table 1

homo- and heteronuclear NMR spectroscopy and by comparison with NMR spectral data available in the literature or published databases [18, 25–27] several categories of chemical compounds were successfully identified in the UPR reference samples, as depicted in Fig. 3. UPR oligomers were identified as a main component of the extracts, comprised of free and esterified phthalate (PhE) or isophthalate (iPhE) and esterified 1,2-propylene glycol (PG) units. Also, propylene glycol units bearing a hydroxyl end group, e.g. either primary (PGm) or second-

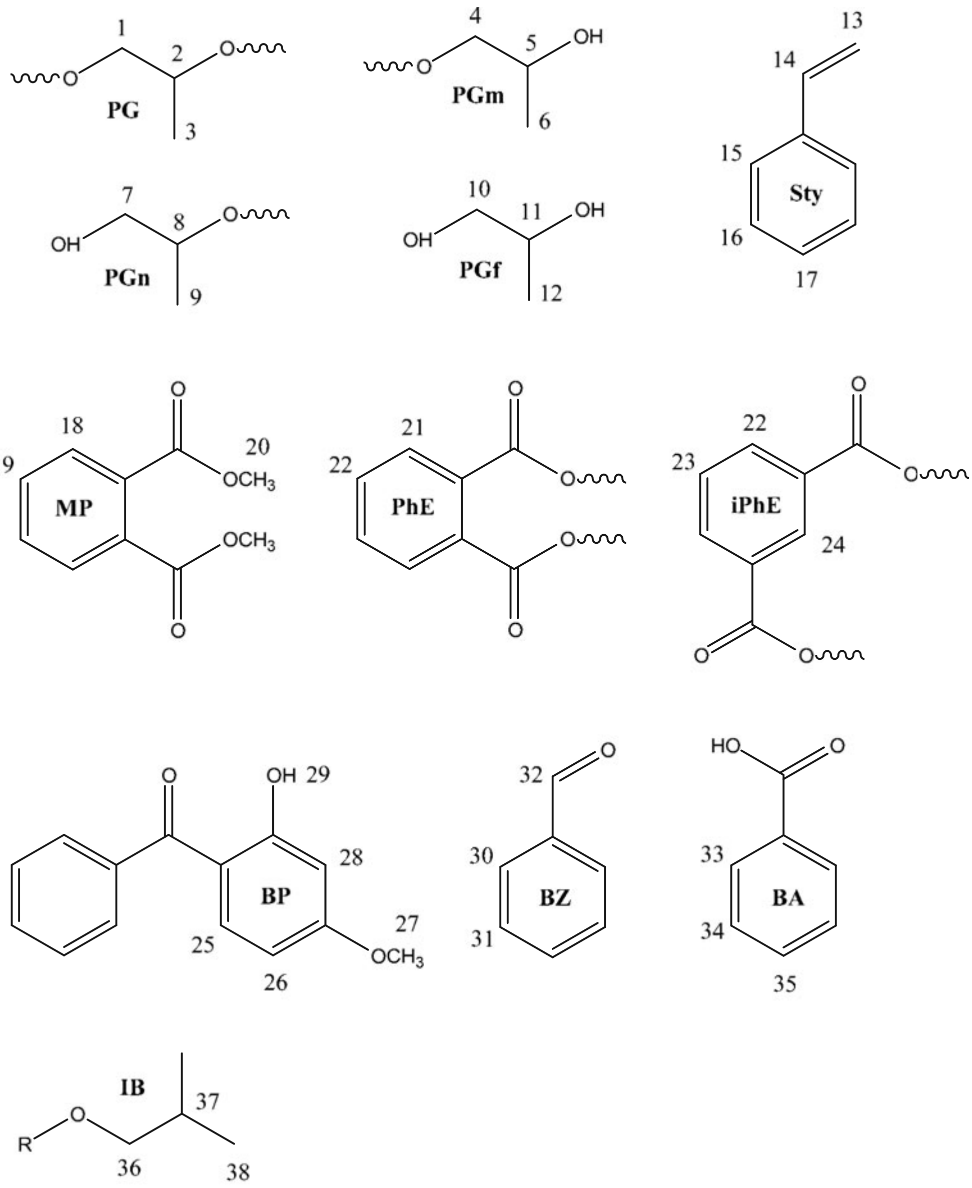


Fig. 3 Structure of the chemical compounds and oligomer units identified in the acetone extracts of two art installations constructed by UPR and reference UPR samples. *PG* diesterified propylene glycol, *PGm* primary –OH propylene glycol, *PGn* secondary –OH propylene glycol, *PGf* propylene glycol, *Sty* styrene, *MP* methyl phthalate, *PhE* phthalate, *iPhE* isophthalate, *BP* 2-hydroxy-4-methoxy-benzophenone, *BZ* benzaldehyde, *BA* benzoic acid, *IB* isobutyl ester or ether unit

ary (PGn) propylene glycol, were identified in all the UP resin formulations studied. Small quantities of fully hydrolyzed PGf were only observed in the spectra of UPR sample A. With respect to low molecular weight compounds, styrene (Sty), dimethylphthalate (MP), benzaldehyde (BZ), benzoic acid (BA), and 2-hydroxy-4-methoxy-benzophenone (BP) were unambiguously identified in the UPR NMR spectra. Styrene is used as the crosslinking agent in the second step of the polymerization reaction that produces the hardened final UPR formulations [3, 4], and its presence as a residual in UPR formulations is well known and studied, because of its toxic effects. Benzaldehyde, a well-known byproduct of the styrene copolymerization reaction, is formed by double bond cleavage on the styrene side chain and can be further oxidized to benzoic acid [28]. Sty and BZ are the two main odor-causing compounds emitted from polyester systems. MP, which is a well-known plasticizer [29] is a component of the peroxide initiator mixture used for crosslinking. Resin formulations A, B, and C were identified as *ortho*-phthalate UPR from their NMR spectra, while resin D was evidently an isophthalate. Furthermore, 2-hydroxy-4-methoxy-benzophenone was identified in the ^{1}H 1D and 2D NMR spectra of cured (C) and aged (C*) UPR, (peaks 25–29 in Fig. 2a). This compound is used as a UV light stabilizer in several commercial resin applications, [3, 29] and verified resin manufacturer information that resin C was light stabilized. Finally, several peaks appear in the aliphatic region of the UPR spectra (0.5–2.5 ppm), that are attributed to aliphatic esters that are included in the peroxide initiator used during polymerization, as verified by manufacturer-

Table 1 Chemical shifts (δ) of the main resonances in the ^{1}H and ^{13}C NMR spectra of the acetone-d_6 extracts of standard UPR resins and two contemporary art installations constructed by UPR

Group	Peak	δ(ppm)	
		^{1}H	^{13}C
PG	1	4.46	67.8
	2	5.46	70.6
	3	1.43	16.6
PGm	4	4.16	71.5
	5	4.07	65.8
	6	1.18	20.0
PGn	7	3.66	65.4
	8	5.14	74.1
	9	1.30	16.5
PGf	10	3.38	68.3
	11	3.74	70.5
	12	1.06	19.4
Sty	13	5.23, 5.80	114.1
	14	6.76	137.9
	15	7.46	127.0
	16	7.33	129.4
	17	7.26	128.7
MP	18	7.75	129.7
	19	7.66	132.0
	20	3.85	52.8
PhE	21	7.77	129.9
	22	7.63	132.3
iPhE	23	8.26	134.7
	24	8.67	131.3
BP	25	7.46	135.6
	26	6.52	108.2
	27	3.91	56.5
	28	6.55	102.1
	29	12.67	–
BZ	30	7.93	130.2
	31	7.63	130.4
	32	10.05	–[a]
BA	33	8.04	130.1
	34	7.51	129.2
	35	7.62	133.2
IB	36	4.06	72.2
	37	–[b]	28.6
	38	0.98	19.4

[a] The peak of the aldehydic quaternary carbon 32 is too weak to be observed in the ^{13}C NMR spectrum

[b] The peak of proton 37 is buried under the intense acetone solvent peak at δ ~2.0

provided product data sheets. The ^{1}H and ^{13}C NMR chemical shifts of all chemical compounds and groups identified in UPR acetone-d_6 extracts are reported in Table 1.

Curing and aging of model UP resins

UP oligomers are formed through ester bond scission, as a result of aging of the original three-dimensional macromolecular matrix formed by crosslinking with styrene. One of the striking features of Fig. 2a is the identification of significant amounts of residual styrene (peaks 13–17) in the UP resins after the curing procedure is finished. This observation indicates that complete curing of the resins is not achieved by the curing procedure applied by the artists when constructing the original art installations. After the UVB aging procedure has been concluded (Fig. 2a, D*, C*) styrene is almost completely evaporated from the UP resin surface. It is understood that when curing is incomplete the initial phase of aging plays the role of an extended curing phase, during which residual styrene continues to evaporate and react with the UPR prepolymers [3, 4].

The concentration of methyl phthalate (peak 20) is also reduced after aging, but MP is still present in relatively large amounts in all aged UPR samples. Both compounds have low boiling points, and contribute significantly to the degradation of the macromolecular polyester matrix, by creating voids through evaporation that allow water to penetrate into [30, 31]. Table 1 summarizes the ^{1}H and ^{13}C NMR chemical shift data of the main chemical moieties that were assigned in the spectra of Fig. 2, with the aid of 2D NMR spectroscopy. After integration and normalization to the number of protons contributing to each peak integral, semi-quantitative data on UPR solvent extract composition at the molecular level are obtained from the NMR spectra both before and after UVB aging. The molar ratios of all chemical entities identified in the UPR extracts (see Fig. 3) are reported in Table 2. All numbers are calibrated to the signal of internal TMS, which was the same in all NMR samples. For some species, integration results were obtained from several equivalent proton peaks, and thus standard deviations are also provided.

ANOVA for the variables of Table 2 was performed in order to elucidate the differences in the chemical composition of the UPR formulation extracts in both the cured and the aged state. ANOVA showed that styrene (F=20.7, $p<0.004$) and benzaldehyde (F=17.3, $p<0.006$) were the two most significant parameters that allow differentiating between cured and aged samples. When the reference samples were grouped according to their origin (A, B, C, D), ANOVA showed that phthalates PhE (F=24.4, $p<0.005$) and the propylene glycol content of the resins PG (F=29.4, $p<0.006$), PGn (F=17.4, $p<0.009$) and PGm (F=10.3,

$p<0.024$) were the most successful parameters in differentiating between different UPR resin formulations.

Figure 4 presents a plot of the amounts of free and esterified phthalates (PhE), total propylene glycol units P (PG+PGm+PGn) and free –OH containing units Pf (PGm+PGn) for all the UPR samples studied in the present report. It is evident that resin samples C and C* contain quite larger amounts of PhE and total PG units in their extracts, indicating that the amount of polyester oligomers extracted from these two samples is significantly higher than the other three UPR formulations. Since sample C has not been subjected to any aging this behavior must be associated to the specific chemical composition of the resin. The presence of large amounts of free –COOH and –OH units (PGm, PGn) in resin C implies that this resin must be more susceptible to osmotic cracking, as it is well known that polar groups increase the hydrophilic character of UPR resins [32]. Furthermore, it is worth noting in Table 2 that in cured UPR resins, the order of concentrations is Sty>>BZ>BA, while in aged UPR resins it becomes BA>Bz>Sty. The latter coincides with the relative boiling point order of the compounds (249, 178, 145 °C), highlighting the role of BZ and Sty as the main volatile organic compounds (VOCs) in UPR resins [28]. As expected, the UPR samples obtained from the two art installations that have been aged for more than 20 years, were also found to be enriched in BA (BA~2BZ) and to contain no detectable amounts of Sty.

PCA and HCA were used in order to visualize the discriminating ability of the NMR-derived parameters of Table 2. Both of these multivariate analysis methods were chosen on purpose because they are unsupervised, namely classification is attempted without any a priori knowledge of the nature of the samples. The plot of the first two principal components extracted from the raw data of Table 2 is depicted in Fig. 5a. It is evident that cured and aged samples form separate groups, while samples C and C* are easily differentiated from the other three UPR resins. The samples from the two installations examined in this report, Cocotte with Two Dogs (CTD) and The Last Milk Platform (TLMP) fall between the aged group and the C group. An almost identical picture emerges when using HCA for the visualization of similarities between the different UPR formulations, as depicted in Fig. 5b, with the samples forming clusters similar to those observed with PCA. Both multivariate techniques indicate that CTD and TLMP samples bare strong compositional similarities to UP resin C.

Mechanical studies

It is known that distresses caused by outdoor weathering conditions are weakening unsaturated polyester products [24] and in particular art installations created with UPR

Table 2 Chemical composition (molar ratios, arbitrary units) of oligomers[a] and organics in acetone-d_6 solvent extracts of standard UPR formulations (A, B, C, D) before and after UVB aging (*), and of two original art installations (CTD, Cocotte with Two Dogs; TLMP, The Last Milk Platform) constructed by UPR resins, as measured by ^{1}H NMR spectroscopy

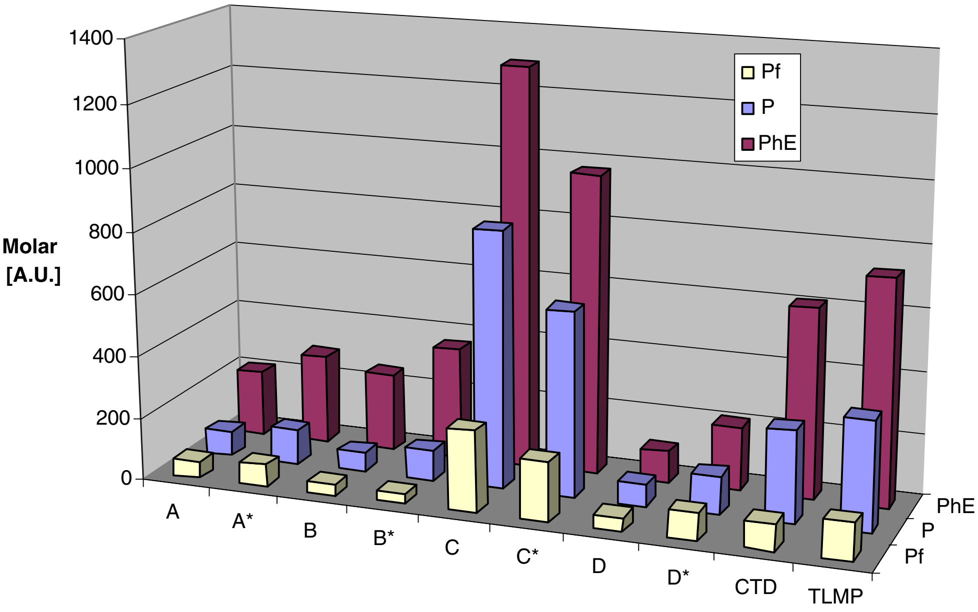
	A	B	C	D	A*	B*	C*	D*	CTD	TLMP
BZ	99.7 (9.7)	51.9 (20.9)	39.5 (13.0)	66.8 (9.5)	3.2 (1.2)	13.5 (2.7)	9.5 (4.3)	12.2 (0.4)	6.5	6.1
BA	52.3	9.4	33.4	40.8	24.3	18.7	10.3	28.7	13.1	13.4
PhE	290.4	361.7	969.2	208.0[a]	213.0	251.1	1291.4	101.4[a]	612.0	728.2
Sty	682.7	714.5	197.2	605.8	2.1	16.3	0.0	0.4	0.0	0.0
MP	103.1	59.3	69.7	51.9	61.2	81.3	79.8	33.0	0.0	0.0
PG	39.6	65.0 (5.3)	405.3 (2.1)	37.3	24.7 (0.3)	25.8 (0.5)	565.0 (7.0)	28.1	210.3 (12.0)	237.0 (19.1)
PGn	16.5 (2.0)	15.3	73.2 (15.5)	29.6	17.7 (3.1)	7.4	106.7 (9.8)	31.9	42.2 (7.6)	61.6 (3.5)
PGm	55.5 (9.8)	16.7	117.9 (9.8)	58.9 (7.2)	36.8 (5.9)	29.7	156.7 (15.5)	11.9 (1.2)	44.8	56.2

Standard deviations are given in parentheses when available

BZ benzaldehyde, *BA* benzoic acid, *PhE* phthalate, *Sty* styrene, *MP* methyl phthalate, *PG* diesterified propylene glycol, *PGn* secondary –OH propylene glycol, *PGm* primary –OH propylene glycol, see Fig. 3

[a] For samples D and D*, PhE refers to isophthalate units

Fig. 4 Plot of the molar quantities (a.u.) of phthalates (*PhE*), total (*P*) and free-OH containing (*Pf*) propylene glycol units for all UPR standard samples (cured, UVB aged) and two original works of art (CTD, TLMP)



[9, 11]. The purpose of the mechanical tests conducted was to clarify the extent of degradation and mechanical properties deterioration effected by different aging conditions to the standard polyester resins studied in this report. The results of breaking strain measurements (ISO 527-2) of unsaturated polyesters tested in three different aging protocols: moisture, freezing/melting and UVB radiation (SFS EN ISO 11507) are reported in Table 3. The breaking strain of the samples, which were under distress, was compared to the samples that were not put under any strain. Inspection of Table 3 shows that UVB radiation has a significant effect on the strength of all the tested UPR reference samples, with sample C being the one most affected. Humidity and heating/cooling cycles on the other hand affected significantly only the strength of UPR resin C, Norpol 450–500, and not the other UPR formulations. In general, the mechanical data show that UPR resin C is the one most susceptible to the deteriorating effects of aging, a conclusion corroborated by the NMR analysis data presented earlier in this report. This analysis showed that the oligomeric material extracted from UP samples C and C* was much higher than the other three resins, and contained almost five times more free –OH units compared to resins A, B, D after curing (Fig. 4). The presence of free polar groups increases the hydrophilic character of the UPR surface facilitating osmotic cracking and promoting further the hydrolytic degradation of the polyester chains.

It is interesting to note (Table 3) that UPR formulation C also contains the lower amount of styrene in the original commercial formulation compared to the other UPR products. Recently it was shown that UPR resins of low styrene content possess inferior mechanical properties compared to traditional UPR [33, 34], and this has been attributed to two separate effects. First, the reduction in styrene content requires a reduction in the molecular weight of the polyester pre-polymer to maintain low viscosity of the formulation prior to crosslinking. This increases the number of free polar end groups (–COOH, –OH) in the final product that are available to interact with water during aging, with the higher water absorption leading to more facile osmotic cracking of the UPR formulation [32, 35]. A second effect is that a low styrene content UPR contains more polyester, leading to higher ester bond concentration in the crosslinked UPR, and thus increasing the possibility of degradation through hydrolytic chain scission of ester bonds [30]. Polyester hydrolysis can induce embrittlement in fiber-reinforced copolyester composites exposed to wet environments through network destruction and/or osmotic cracking [31]. Recently, it was reported that reduced styrene emission polyester resin composites are more brittle than traditional UPR formulations [36], suffer from easier mechanical damage initiation and propagation, and are more prone to fail under stress [37].

In summary, it appears that the low tolerance of UPR C to various aging treatments could be attributed to its lower styrene content, compared to the other three standard UPR formulations. It is interesting to note that before aging all four UPRs have similar mechanical properties (Table 3). This observation stresses the importance of aging studies to determine the suitability of plastics for use as cultural heritage materials, since performance shortfalls can be masked in "fresh" polymeric resin formulations.

An important note of interest emerges when it is considered that resin C was the only one of the four UPR materials studied that contained a benzophenone UV light

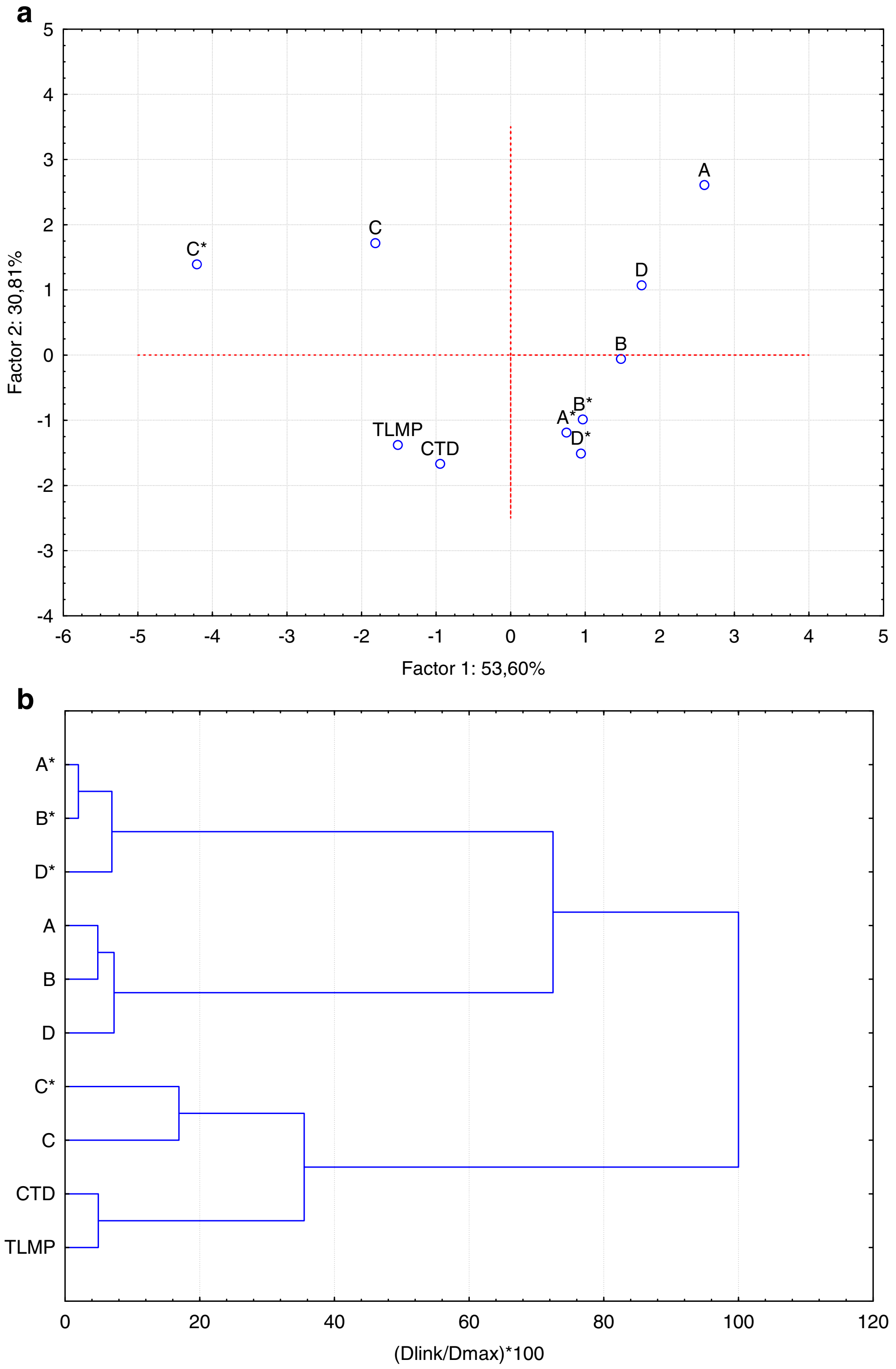


Fig. 5 **a** Principal component analysis scores of the UPR samples and the two original works of art (CTD, TLMP) for the two first factors extracted from the experimental data of Table 2. **b** Hierarchical cluster analysis tree diagram of the UPR samples

stabilizer additive, as verified previously by NMR spectroscopy. Although resin C suffered significantly less yellowing after UVB aging compared to non-stabilized samples [20], it still possessed inferior mechanical properties after UVB aging (Table 3), its breaking strain being almost half of that of the other three reference UPR samples. Thus, it appears that although UV light stabilization is important to maintain the external optical properties of art installations constructed by UPR or protected with UPR topcoats, it has no effect on the degradation characteristics and the deterioration of UPR mechanical properties during aging.

Table 3 Breaking strain results (N/mm^2) of UPR reference samples before and after exposure to various aging conditions

Resin product	Sample ref.	% Styrene	Cured	Moisture (63 days)	Melt/Freeze (30 times)	UVB (641 h)
Synolite	A	46±2	39.2±4	39.9±2	38.1±3	20.8±2
Norpol 540–800	B	43±2	41.4±1	41.5±1	39.4±2	20.8±4
Norpol 450–500	C	34±2	40.9±5	18.3±4	14.6±5	11.6±3
Norpol 720–700	D	44±2	42.9±2	39.1±1	36.7±1	22.7±2

"Cocotte with two dogs" and "The last milk platform"

Figure 6a compares the ^{1}H NMR spectra of the organics extracted from samples from the two original art installations, CTD and TLMP, with that of aged resin C*. The three spectra have almost identical features indicating that the UPR resin C or a compositionally very similar resin has been used in the construction of these two works by the respective artists. The main phthalate and propylene glycol peaks are indicated on the proton spectrum of CTD in Fig. 6a. This compositional similarity is further supported by the comparison of the ^{13}C NMR spectra of samples C* and CTD, presented in Fig. 6b, where the carbon peaks on the CTD spectrum are also assigned. It should be noted that the compositional similarity between resin C and the two art installations was also suggested by the statistical analysis of the UPR samples using PCA and HCA methodologies.

The ^{1}H and ^{13}C NMR spectra of CTD and TLMP contain a few additional peaks, compared to resin C*. Two proton peaks at δ 0.984 and 4.06 where assigned via 2D NMR spectroscopy to an isobutyl ester or ether (IB) moiety (Fig. 3), and this was supported by the ^{13}C NMR spectrum of CTD, where the respective carbons (C36–38) have also been assigned (Fig. 6b). Since methyl phthalate plasticizer was not detected in the extracts of the two artworks studied in this report, these peaks should probably be attributed to isobutyl phthalate, which is a well-known plasticizer for plastics and polymers [29]. Additionally, a broad feature appears in the aromatic region (δ 6.9–7.4) of the ^{1}H NMR spectra of the samples from the two works of art in Fig. 6a. This feature is barely visible in the proton spectrum of aged C*, and is most probably attributed to polystyrene (PS) fragments included in the resin oligomers produced during UPR degradation. The presence of PS fragments is expected for UPR materials that have suffered from heavy weathering, such as the two art installations that have been exposed to high humidity and extreme temperatures as a result of being exhibited outdoors for several years. Extended degradation increases the possibility that larger fractions of polymeric chains that contain PS fragments are being chopped off the three-dimensional macromolecular network created during crosslinking. This advanced degradation state is also evident in Fig. 4, where CTD and TLMP appear to contain larger amounts of phthalate and propylene glycol oligomers in their acetone extracts, compared to aged samples from all the other three resins (A*, B*, D*), in agreement with results obtained by macroscopic and visual examination of specimens from the two art installations [20].

Conclusions

The high-resolution NMR spectroscopy results presented in this report demonstrate the potential of this methodology as an analytical tool for the study of polymeric materials used in contemporary artworks. Apart from the ability to identify the chemical composition (e.g., phthalate/isophthalate, type of glycol, plasticizer, additives, etc.) of a UPR formulation, when aided by suitable reference samples NMR spectroscopy can pinpoint the exact commercial product used as construction material in an art installation, i.e., the use of UPR C in the two art installations studied in the present report. The analysis of the organics present in the solvent extracts of UPR materials provides important information regarding the degradation state of the macromolecular UPR network, including the quantities of free –OH groups. The composition of the extracts can be used to aid in the differentiation between various UPR formulations and facilitate the identification of original works of art based on their aging condition.

Furthermore, several important points regarding the aging behavior and degradation state of UPR resins as art materials were drawn. It was shown that care must be taken by artists so that complete curing of the UPR-constructed artifacts has been affected. Evidence was provided that low styrene content UPR products, although preferable in terms of environmental concerns due to lower VOC emissions, might be associated with inferior mechanical properties, such as increased brittleness and reduced resistance to hydrolysis. Such properties facilitate polymer degradation and may reduce the useful lifetime of

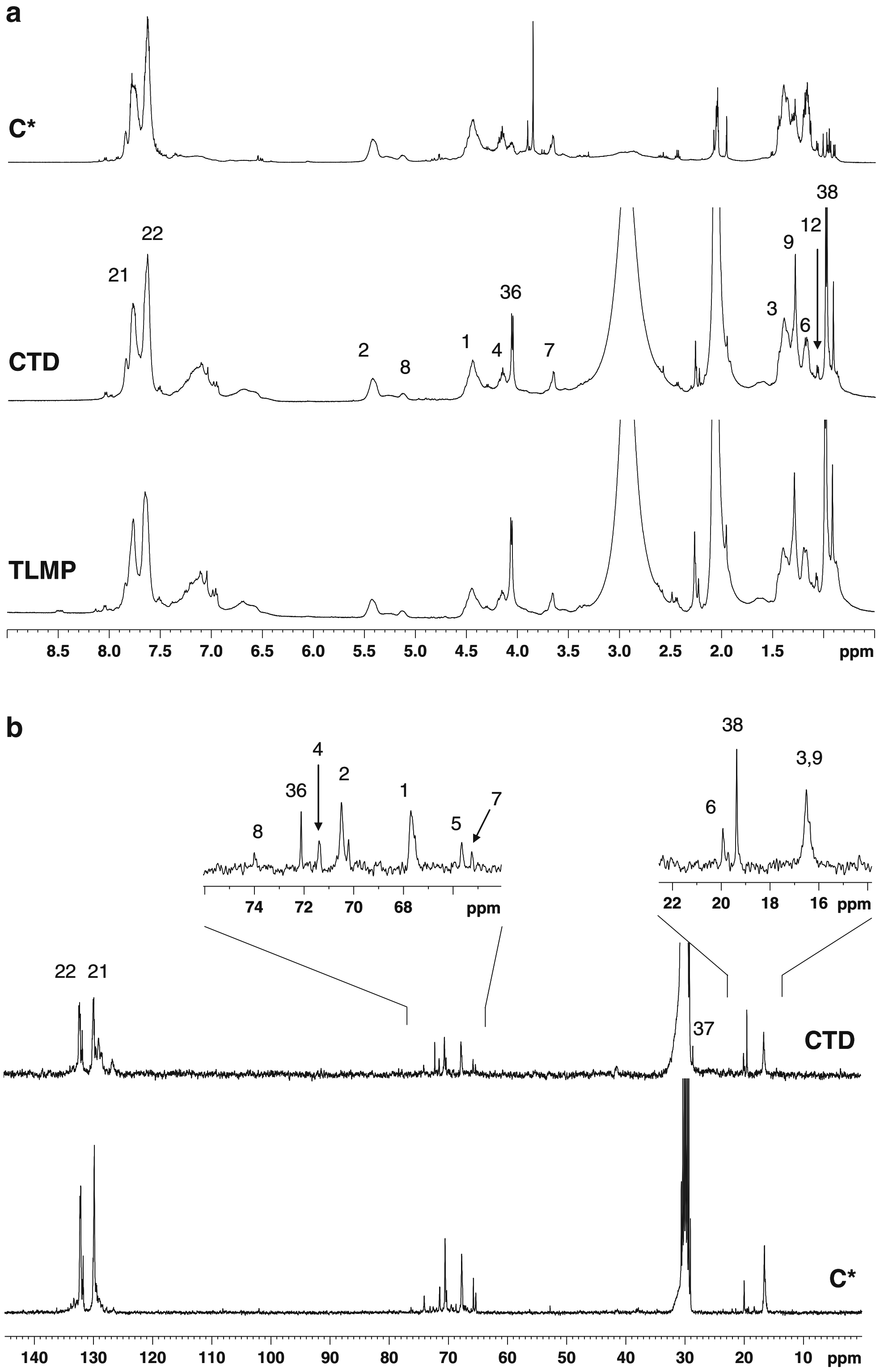


Fig. 6 **a** ^{1}H NMR spectra of acetone-d_6 extracts of aged sample C*, and two samples obtained from the artworks Cocotte With Two Dogs (*CTD*) and The Last Milk Platform (*TLMP*). **b** ^{13}C NMR spectrum of acetone-d_6 extracts of aged sample C* and one sample from Cocotte With Two Dogs (CTD)

artifacts containing them as structural components and necessitate increased efforts during conservation and restoration work.

Finally, it is worth noting that although the NMR spectroscopic approach (using either liquid extracts or solid samples) necessitates micro-sampling of the artwork, unlike non-invasive magnetic resonance methodologies using surface coils [38], this seems to be more than compensated by the rich chemical information obtainable from 1D and 2D NMR spectroscopic data.

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