

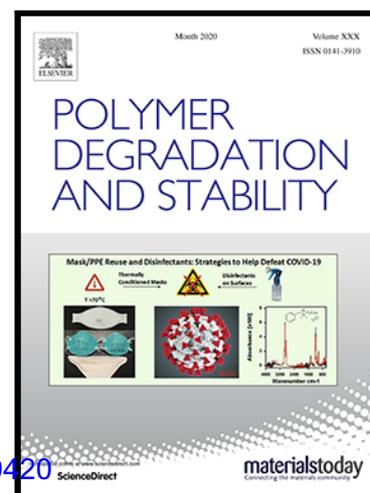
Characterising plasticised cellulose acetate-based historic artefacts by NMR spectroscopy: a new approach for quantifying the degree of substitution and diethyl phthalate contents

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Highlights

- ^1H NMR for measuring plasticiser loss in cellulose acetate-based historic artefacts
- Degree of substitution determination in plasticised cellulose acetate by ^1H NMR
- Assessment of cellulose acetate-based historic artefacts degradation using ^1H NMR

Journal Pre-proof

Characterising plasticised cellulose acetate-based historic artefacts by NMR spectroscopy: a new approach for quantifying the degree of substitution and diethyl phthalate contents

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ABSTRACT: As one of the first semi-synthetic plastics produced industrially, cellulose acetate (CA)-based artefacts represent valued items in museum collections and archives which, however, present stability issues. High temperature and relative humidity conditions have long been known to promote changes in CA properties, for instance, due to the deacetylation of CA polymer chains and the loss of plasticiser from the polymer matrix. However, there is a need for improved methods for the quantification of plasticiser loss and CA deacetylation. In this context, this contribution presents a new approach for enabling the investigation of plasticiser loss and deacetylation degradation processes in historic plasticised CA-based artefacts which is based on high-resolution proton nuclear magnetic resonance spectroscopy (^1H NMR). The proposed methods allow for simple and fast quantification of diethyl phthalate contents and average degree of substitution (DS), while requiring no need for extractive separation between the plasticiser and the CA polymer matrix prior to analysis. Both methods are demonstrated by their application towards a series of reference samples, historic artefacts and artificially aged plasticised CA materials. Our analysis indicates that plasticiser content and DS can be accurately quantified by using high-resolution ^1H NMR and both methods have been compared to analyses performed using infrared spectroscopy.

Keywords: cellulose acetate; stability; NMR spectroscopy; plasticiser loss; deacetylation; degree of substitution.

1. Introduction

Cellulose acetate (CA) is a polymer derived from the acetylation of cellulose which finds industrial applications in a wide range of fields, including the production of cigarette filters, textile and fibers, plastics, coatings, photographic films, protective films in liquid crystalline displays, adsorbents and membranes for separation applications [164].

As one of the first semi-synthetic plastics produced industrially in the early 20th century and owing to the social impact caused by the advent of polymers, many CA objects, including the sculptures made by Naum Gabo, Antoine Pevsner and László Moholy-Nagy, are collected, conserved and cared for in museum collections and archives, as iconic and valued representations of the past. However, many of these materials present stability issues associated with their chemical and physical degradation, imposing a challenge for conservators in the search for optimal storage and display conditions [568].

Both the loss of plasticisers and deacetylation have been described as important processes associated with the loss of structural integrity and aesthetic value of CA art objects [9,10]. Whereas the loss of plasticisers may be linked to physical changes such as warping, crazing, cracking and brittleness [11], the deacetylation of CA chains as a product of hydrolysis is associated with the formation of acetic acid and its release to the environment, resulting in a characteristic vinegar-like odour in the vicinity [12].

Given the potential negative impact of these processes on the aesthetic or information value, developing suitable analytical methods for investigating these processes and their relationship with storage conditions is of paramount importance for protecting cultural heritage, to either expand the life time of artefacts, determine when restoration must take place or define when storage and display conditions must be changed.

Different analytical methods have been proposed for investigating plasticiser loss from CA based materials, for which diethyl phthalate, dimethyl phthalate, triphenyl phosphate and their mixtures are commonly used as external plasticisers [13,15]. Usually, suitable solvents are employed to extract and separate plasticisers from the CA polymer matrix, allowing for the analysis of the solvent-plasticiser solution by either high performance liquid chromatography (HPLC) [13], gas chromatography [16,18] or gravimetry [19]. Alternatively, the weight loss from the polymer phase after extraction has also been used to quantify plasticiser contents [20,21]. In the absence of extraction procedures, plasticiser contents have also been quantified directly in the plasticised CA matrix by either thermogravimetry [1,20,22] or infrared spectroscopy [1,22].

The deacetylation process, in turn, can be studied by quantifying the average degree of substitution (DS), defined as the average number of acetyl substituent groups per anhydroglucose unit (AGU) in the CA molecular structure [23]. For this purpose, a saponification reaction followed by titration of the unreacted NaOH with an acid is a standard recommendation [24,26]. The quantification of the CA saponification product by ion chromatography [17] and additional derivatisation methods, involving the aminolysis of CA followed by gas chromatography-mass spectrometry analysis [20], have also demonstrated promising performance for quantifying DS.

Whereas both plasticiser loss and deacetylation processes can be indirectly monitored by using the above-mentioned methods, the extractive separation of plasticiser and the CA matrix can lead to long analysis times (days) and involve multiple extraction cycles [17]. On the other hand, the use of plasticised CA in infrared spectroscopic studies may be limited to reference materials, due to the superposition of vibration bands for similar phthalates.

In this context, the use of nuclear magnetic resonance (NMR) spectroscopy represents an efficient alternative to overcome the above-mentioned drawbacks, as the requirement for

plasticiser removal and separation from the polymer matrix can be excluded, as previously demonstrated for the quantification of plasticisers in polyvinyl chloride (PVC)-based medical devices [27]. In addition, while the initial sampling procedure requires an interventive approach with respect to the original object, this analysis technique presents the advantage of involving simple sample preparation, requiring minute amounts of sample from the object and enabling further investigation of the dissolved sample after analysis, which can represent a critical characteristic when access to original material from artefacts is limited, as also pointed out by [28]. However, despite being very common in the field of chemistry, the use of NMR spectroscopy for quantifying polymer degradation processes in the heritage field, particularly in polymeric modern and contemporary art pieces, remains underused.

For instance, high-resolution liquid NMR spectroscopy has been applied to the characterisation of the state of hydrolysis and oxidation of oil painting in works of art by mono- and diglycerides, and the formation of free fatty acids as a result of hydrolysis [28,29]. Identification and semi-quantitative analysis of the chemical composition of solvent extracts from contemporary art installations based on unsaturated polyester resins has also been demonstrated [30]. Solid-state cross-polarization magic angle spinning (CPMAS) NMR spectroscopy has also been employed in the characterisation of poorly soluble materials, such as ancient natural rubber [31], historical collagen-based parchments [32], oriental lacquers and amber [33], whereas more recently, portable unilateral NMR sensors (NMR-MOUSE) have been successfully used in the quantification of moisture in wall paintings [33,34], plasticisers in PVC [35], and in the monitoring of ageing processes in historic hard rubber [36], low-density polyethylene [37], in addition to other historically significant materials including paper and paintings [38-40].

However, in studies involving historic cellulose acetate artefacts, to the best of our knowledge, high-resolution NMR spectroscopy has been employed only as a qualitative tool for the identification of additives [41], or as a quantitative method for characterising DS in unplasticised, commercial CA samples [42], by using promising ^1H and ^{13}C NMR methods previously developed for unplasticised CA [4,43,46]. In this context, while quantitative ^{13}C NMR may present promising performance for quantifying average DS and even allow for the determination of the acetyl distribution in unplasticised CA [46], its use may be complicated by the low natural abundance and low gyromagnetic ratio of the ^{13}C nucleus, which yields much smaller sensitivities when compared to ^1H NMR [27,47], and also present the drawback of requiring longer analysis times, due to the long relaxation times and required high temperature [46]. However, the use of high-resolution ^1H NMR spectroscopy for quantifying diethyl phthalate (DEP) contents and DS values in plasticised historic CA materials which we report in this paper, including rigorous characterisation of errors from replicated measurements and demonstrated characterisation of spin-lattice relaxation times, has not been reported.

Therefore, this contribution demonstrates for the first time how DEP contents in CA can be quantified using high-resolution ^1H NMR spectroscopy while requiring no need for separation between the plasticiser and the CA polymer matrix prior to analysis. In addition, we propose a method for characterising the average degree of substitution of DEP-plasticised CA, also by using high-resolution ^1H NMR spectroscopy and requiring no plasticiser removal. Both methods are demonstrated by their application towards a series of reference samples, historic artefacts and artificially aged plasticised CA materials. Our analysis indicates that plasticiser content and CA average degree of substitution can be accurately quantified by using high-resolution ^1H NMR and results from both methods have been compared to results obtained by infrared spectroscopy. We envisage this new approach will

prove useful in qwt"cpf"qj gtuø'continued efforts to determine the effect of aging conditions qp"ECa"chqrementioned degradation processes.

2. Materials and methods

2.1 Synthesis of plasticised cellulose acetate

Cellulose acetate (CA) with an average degree of substitution (DS) equal to 2.45 ± 0.05 and diethyl phthalate (DEP) (99.5 %) were purchased from Sigma Aldrich (London, United Kingdom). The purchased CA will be referred to in this text as *Commercial CA*. Plasticised CA samples were prepared using the solvent casting method. To obtain miscible blends and avoid phase separation [14], the amount of plasticiser added was tailored to result in final materials containing no more than 22 wt% of plasticiser. In a typical procedure, plasticised CA containing 20 wt% of DEP was prepared by dissolving DEP (24.12 g) in acetone (100 mL) (99 %, Alfa Aesar), before the addition of *Commercial CA* (96 g), which was then followed by the addition of further acetone (200 mL). The resultant mixture was kept under reflux for 4.5 h with continuous stirring, allowed to cool for 1 h with stirring and finally poured over a flat glass tray.

Slow solvent evaporation was allowed for 1 week by keeping a glass lid over the sample tray at room temperature. The final drying procedure was performed in a vacuum oven (150 mbar) for 96 h at 20 °C. Square sample pieces (2 cm x 2 cm x 2 mm) were produced by cutting and samples were stored at 5 °C prior to ageing experiments and between analyses. Throughout this work, these samples are labelled as *x-DEP/CA*, where *x* represents the plasticiser content in wt%.

2.2 Historic samples

Historic plasticised CA materials, as illustrated in the Figure S1 of the Supporting Information (SI), as sheets of five different colours and thickness, were kindly donated by Colin Williamson (CW) and labelled by using the CW initials followed by the colour of the

sheets, as *CW-blue*, *CW-green*, *CW-black*, *CW-brown* and *CW-red*. One additional CA object from the Historic Plastic Reference Collection at the UCL Institute for Sustainable Heritage (HPRC-UCL-SH), named as *HS91* [48], and three historic CA combs, kindly donated by Jen Cruse [49] and labelled as *Comb C1*, *Comb C14* and *Comb C19*, illustrated in Figures S2-S3 of the *SI*, were also evaluated. Finally, two colourful vintage CA pen cases, purchased from private collectors and labelled as *Green Case* and *Blue Case*, Figure S3, were also analysed. Although the manufacturing date of historic samples is uncertain, it is believed that the *CW* *Comb C14* is dated from 1940.

2.3 Thermal ageing of reference and historic materials

Historic and reference CA materials have been thermally degraded at 40, 55 and 70 °C for different lengths of time which varied between 14 and 120 days. Sample pieces were individually suspended within 100 mL sealed *Duran* glass bottles which contained 20 mL of aqueous sodium bromide saturated solution to produce a relative humidity (RH) of 50% [50]. The control of temperature was performed by placing sample bottles in *Carbolite* ovens. Temperature and relative humidity were monitored during the experiments by using *TinyTag Ultra2*[®] dataloggers, which were also individually suspended in sealed glass bottles containing the salt saturated solution and kept in the oven.

2.4 NMR spectroscopy

For all NMR analyses, deuterated dimethyl sulfoxide (*DMSO-*d*₆*, 99.9 atom % D, Sigma Aldrich, London, United Kingdom, used as received) was used as solvent. ¹H NMR spectra were recorded at 298 K on a Bruker Avance Neo 700 MHz NMR spectrometer equipped with a helium-cooled broadband cryoprobe, using a standard single pulse experiment with a 30° pulse (zg30 in the standard library of Bruker NMR pulse sequences). The acquisition time was 4 s and the number of scans was equal to 32. Fourier transformation

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8. Authors contributions statement

Simón Da Ros: Conceptualization, Methodology, Formal Analysis, Investigation, Writing - Original Draft, Writing - Review and Editing. **Abil E. Aliev:** Methodology, Writing - Review and Editing. **Isabella del Gaudio:** Methodology, Writing - Review and Editing. **Rose King:** Methodology, Writing - Review and Editing. **Anna Pokorska:** Methodology, Writing - Review and Editing. **Mark Kearney:** Methodology, Writing - Review and Editing. **Katherine Curran:** Conceptualization, Methodology, Formal Analysis, Writing - Review and Editing, Funding Acquisition.

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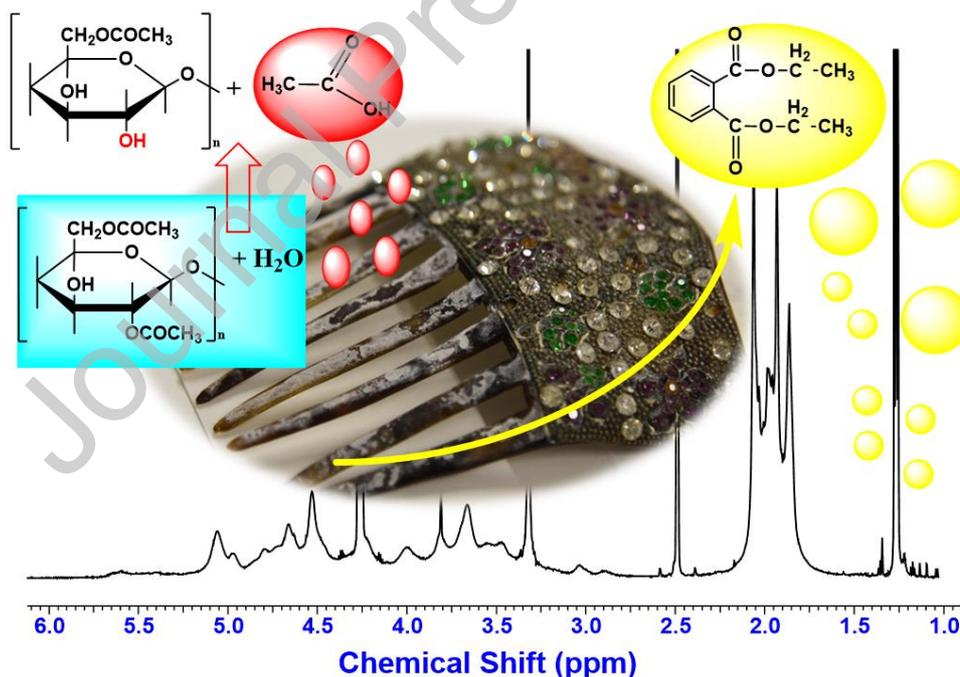
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