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Characterization of acrylic resins used for restoration of artworks by pyrolysis-silylation-gas chromatography/mass spectrometry with hexamethyldisilazane☆

Laura Osete-Cortina, María Teresa Doménech-Carbó *

Dpt. Conservation and Restoration of Cultural Goods, Heritage Conservation Institute, Polytechnical University of Valencia, Camino de Vera 14, 46022 Valencia, Spain

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Abstract

A procedure based on the technique of the pyrolysis-GC/MS has been applied, in this work, in order to determine the composition of synthetic acrylic resins employed in artworks. The method is based on the on line derivatization of these resins using hexamethyldisilazane (HMDS). Results obtained have been compared with those others from direct pyrolysis and *in situ* thermally assisted hydrolysis and methylation with tetramethylammonium hydroxide (TMAH). Sensitivity using HMDS as derivatising reagent is found similar to that from direct pyrolysis and methylation with TMAH. Better resolution of the most representative peaks has been also obtained. Additionally, this method reduces the formation of free acrylic acid molecules during the pyrolysis process and, in consequence, more simplified and well-resolved chromatograms are obtained. Finally, the reported procedure has been successfully used for characterizing several acrylic-based varnishes and binding media currently used in Fine Arts and real pictorial samples from graffiti performed on a Middle Ages bridge.

Keywords: Py-GC/MS; Acrylic resin; Varnish; Binding medium; Adhesive; Consolidant; Artwork; HMDS; TMAH

1. Introduction

Identification of organic materials used as protective coatings and binding media are important matters of study for the scientists that are helping with the work of conservation, due to their higher degree of reactivity if it is compared to that of inorganic materials also present in the art object such as pigments, inerts and grounds. Thus, organic compounds are prone to undergo deterioration processes which can endanger the integrity of the art object. Characterization of materials and identification of deterioration processes affecting them is critical to a full understanding of the reasons for their corrosion or deterioration and the determination of the appropriate treatment and storage environment.

The history of synthetic polymers for artistic purposes began after the invention by Schönbein of the first synthetic polymer, cellulose nitrate, in 1899 [1]. A few years later, Alexander Parkes displayed moulded cellulose nitrate objects at the International Exhibition in London. In the 20th century, synthetic polymers have almost replaced the application of traditional natural resins in art and in the restoration of archaeological objects due to their excellent physical properties and special functionalities. Their wide variety of formulations make these materials very useful as varnishes, media, consolidants and adhesives for paintings or fillers of missing parts used in restoration works for stone materials and archaeological objects among others. Differentiation of these synthetic polymers used in former restoration works from the original materials used by the artist is also of great interest to establish an adequate restoration process. However, differentiation of these materials is a great challenge because of the small variations in formulations and the presence of a multitude of additives in the synthetic resins commercially available.

Acrylic resins obtained in 1901 by Röhm started to be employed as paint medium after the second world war as an

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* Corresponding author.
E-mail address: tdomenec@crbc.upv.es (M.T. Doménech-Carbó).

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alternative to alkyd resins and drying oils. Acrylic media usually come in form of a dispersion of a methyl methacrylate–ethyl acrylate (MMA–EA) co-polymer. This medium was frequently used by the artists from the 20th century due to its properties of reduced drying time and low yellowing. Other acrylic resins such as ethyl methacrylate–methyl acrylate (EMA–MA) co-polymer, and poly *n*-butyl methacrylate (nBMA) dissolved in organic solvents, are used as varnishes, lacquers, adhesives and consolidants.

A variety of instrumental techniques have been proposed for identifying synthetic polymers used in the field of the conservation of cultural heritage [1–8]. Among others, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) has demonstrated its usefulness for characterizing and identifying acrylic resins used as components of modern media, coatings and components or additives of adhesives and consolidants.

Studies dealing with the analysis of work of art pieces are made difficult, however, by the restriction of sample amounts lesser than the microgram and by the presence of different analytes in the sample. In particular, the analysis of synthetic resins used in the art objects as binding media, varnishes, adhesives, fillers and consolidants may require the resolution of complex mixtures, including both organic and inorganic compounds. Additionally, acrylic resins, as synthetic polymeric materials, generally show a low volatility which makes the application of techniques such as gas chromatography/mass spectrometry difficult. These reasons perform Py-GC/MS as a suitable technique for studying these art materials.

Py-GC/MS has been proposed for the analysis of acrylic resins, present in art and archaeological objects, because of the main advantage of requiring reduced sample amount and treatment [9]. More recently, derivatization associated with the pyrolytic process has been proposed to improve the detection of compounds with polar groups such as carboxylic and hydroxyl groups in the analysis of artwork materials. Thermally assisted hydrolysis and methylation performed with tetramethylammonium hydroxide (TMAH) has been preferably used in the analysis of synthetic resins [10–12]. Nevertheless, other pyrolysis derivatization reagents have probed their efficiency in the analysis of materials used in artworks. An increasing number of reports are found in specialised literature in which trimethylsilyl derivatization reagents are used in analytical pyrolysis of natural polymers. Among other derivatising reagents, bis(trimethylsilyl)trifluoroacetamide has been proposed for the analysis of lignin [13] and cellulose and chitin [14]. Similarly, hexamethyldisilazane (HMDS) has been proposed for the analysis of natural products formed by polar molecules as in the case of proteins [15], lipids [16], carbohydrates [17], dyes [18,19], diterpenoid resins [20,21] and triterpenoid resins [20,22].

The general purpose of the present work was to carry out a study aimed at the improvement of the analytical methodologies previously proposed for the analysis of acrylic resins used in artworks based on Py-GC/MS analysis. Results obtained from the two commonly used derivatization reagents TMAH and HMDS have been compared on a series of commercial art products and standard acrylic compounds. Finally, the proposed method based on the use of HMDS as derivatization reagent has been applied to several contemporary artworks.

2. Experimental

2.1. Solvents and reagents

2.1.1. Analytical reagents

The following reagents were used to treat the samples: hexamethyldisilazane (HMDS) and tetramethylammonium hydroxide pentahydrate (TMAH) (97%) (Sigma, Steinheim, Germany).

Commercial denomination, composition, supplier and main application in the field of conservation of cultural goods of the products analyzed by Py-GC/MS are summarized in Table 1. Attending to their chemical composition the studied commercial products are classified in seven main groups: (a) butyl methacrylate (BMA) type, (b) butyl methacrylate–2-ethylhexyl methacrylate (BMA–2-EHMA) type, (c) butyl acrylate–methyl methacrylate (BA–MMA) type, (d) butyl acrylate–butyl methacrylate–methyl methacrylate (BA–BMA–MMA) type, (e) ethyl acrylate–methyl methacrylate (EA–MMA) type and (f) methyl acrylate–ethyl methacrylate (MA–EMA) type. Additionally, methacrylic acid and acrylic acid, supplied by Sigma–Aldrich, have been used in this work.

2.2. Instrumentation and procedures

Experiments were carried out with an integrated system composed of a CDS Pyroprobe 1000 heated filament pyrolyser (Analytical, New York, USA), and a Gas chromatograph Agilent 6890N (Agilent Technologies, Palo Alto, CA, USA) coupled to an Agilent 5973N mass spectrometer (Agilent Technologies) and equipped with pyrolysis injection system. A capillary column HP-5MS (5% phenyl–95% methylpolysiloxane, 30 m × 0.25 mm I.D., 0.25 μm film thickness, Agilent Technologies) was used in order to provide the adequate separation of components.

Pyrolysis was performed at 700 °C for 10 s, according to the laboratory experimentations detailed in the discussion, using a precalibrated Pt coil type pyrolyser (CDS pyroprobe). The pyrolyser interface and the inlet were set at 250 °C. The samples were injected in split mode (split ratio 1:80). The chromatographic conditions were as follows: initial temperature of 50 °C increased at 5 °C min^{-1} up to 100 °C increased at 15 °C min^{-1} up to 295 held for 2 min. Helium gas flow was set at 1.2 ml min^{-1}. The inlet pressure of the carrier gas was 67.5 kPa. The electronic pressure control was set to constant flow mode with vacuum compensation.

Ions were generated by electron ionisation (70 eV) in the ionisation chamber of the mass spectrometer. The mass spectrometer was scanned from *m/z* 20 to 800, with a cycle time of 1 s. An Agilent Chemstation software G1701CA MSD was used for GC-MS control and mass spectra evaluation. Tuning of the mass spectrometer was checked using perfluorotributylamine (PFTBA).