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Thermal degradation chemistry of archaeological pine pitch containing beeswax as an additive

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ABSTRACT

Thermo analytical techniques and gas chromatography/mass spectrometry (GC/MS) were used to evaluate the presence of chemical-physical interactions between pine pitch and beeswax used as additive The mixtures found in several archaeological objects demonstrate that by modifying the physical and chemical properties of pitch and tar, our ancestors were able to add a variety of organic materials, such as waxes or animal fats. We studied pine pitch replicas from *Pinus sylvestris* prepared following a test from the field of experimental archaeology. Varying proportions of beeswax were added and then the resulting pitches were studied by a multi-analytical approach comprising the use of thermo analytical techniques (DSC, TG and TG-FTIR) and GC/MS, which provides molecular information. The same approach was also used to study a mixture of pitch from *Pinus sylvestris* L. and beeswax ("Zopissa"), whose relative proportions were unknown, and two archaeological adhesives collected from glass *opus sectile* fragments found in the northern necropolis of Antinoopolis (Egypt, 4th–5th century AD). Our thermo-analytical techniques managed to determine the relative proportion of pine pitch and additives, such as beeswax, in unknown archeological mixtures, and to evaluate the presence of interactions between pitch and additives.

1. Introduction

Since early times, the resinous substances secreted by trees have been widely used either in their natural form or as tar and pitch to waterproof the planking of ships and vessels, and as adhesives [1–9]. Tar and pitch have been of great importance in terms of their properties, such as insolubility in water, adhesion and glasslike characteristics.

Tar and pitch were obtained by subjecting resinous materials to hard-heating(pyrolysis)-type processes. The exact methods used for the production of pitch and tar before the use of kilns have not yet been completely clarified. Archaeological and documentary evidence as well as experimental archaeology tests suggest that various methods could have been used [10–12]. The most ancient documentary evidence is *De Historia Plantarum* (4th–2nd century BC) by Teophrastus, who wrote that the Macedonians made huge piles of cloven trunks, covered them with peat and soil, and then burnt the wood, letting the tar and pitch run out in a canal.

During the pyrolysis process to obtain pitch and tar, terpenoids, the main compounds of resins, undergo chemical modifications, such as aromatization, demethylation and decarboxylation. This gives rise to the formation of new compounds with a lower molecular weight and a high degree of aromatization [13]. In addition, during the hard-heating (pyrolysis)-type processes of wood from pine and firs, the formation of methylated diterpenoid acids was established: the high amount of methanol in the gas phase reacts easily with diterpenoid acids to produce, above all, methyldehydroabietate [4,13,14].

The mixtures found in several archaeological objects demonstrate that in order to modify the physical and chemical properties of pitch and tar, a variety of organic materials, such as waxes or animal fats, were added [1,8,15–17]. For example, mixtures of pine pitch, beeswax and *brassicaceae* seed oil were used as adhesives in the manufacture of *opus sectile* and mosaic decorations [15]. In the ancient world, beeswax and *brassicaceae* seed oil were used to change the physical and chemical characteristics of the pine pitch thus allowing more malleable and mouldable adhesives to be obtained. In addition, the fact that brassica oil was used would seem to demonstrate that its semi-siccative properties were already well known in ancient Egypt. All this testifies to the high technological skills of the craftsmen who created the *opus sectile* and mosaic decorations.

In another case, the presence of triterpenoid fatty acyl esters, which are naturally present in birch bark or in tar and pitch derived

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from birch, suggest that an animal fat was intentionally added to birch bark tar to produce a modified adhesive/waterproofing material [16]. The formation of stable bonds between triterpenoids and fatty acids to give the corresponding fatty acyl esters was attributed by our forefathers to mixing and heating processes, suggesting not only an intentional addition but also an advanced technological level [16].

The aim of this work is to evaluate the presence of chemical-physical interactions between pine pitch and beeswax used as additive. Pine pitch replicas from *Pinus sylvestris* were prepared using a procedure from experimental archaeology. Varying proportions of beeswax were added to the replicas and studied by a multi-analytical approach comprising the use of gas chromatography/mass spectrometry (GC/MS) and thermoanalytical techniques (DSC, TG and TG-FTIR). DSC and TG analysis have already been successfully used to investigate archaeological woods [18,19], and have been used to highlight interactions among pigments and fluid binders such as proteins, linseed oils and alkyd resins [20–24]. Consequently, we believe that they could also help us to understand the interaction between pine pitch and beeswax and to give an idea about the relative proportion of pine pitch and beeswax in unknown archaeological adhesives.

The pine pitch used in this study was produced using an autothermal method [12]. GC/MS was used to assess the molecular composition of pitch replica and to identify a series of species acting as markers of technological manipulation and possible degradation. In addition, GC/MS analysis was applied to pine pitch heated up to 300 °C under nitrogen and air flow.

By studying the mixtures of pine pitch with different amounts of additive by thermal analysis we can extend our knowledge of the techniques used in the past. The thermo analytical results of the samples obtained by adding different amounts of beeswax to the pine pitch compared with those of the pure pine pitch and beeswax highlight how beeswax affects the pitch and the results also reveal the presence of possible pine pitch/beeswax interactions.

The same approach was also used to study a mixture of pitch from *P. sylvestris* L. and beeswax "Zopissa" (furnished by Dr. Andreas Kurzweil, Arbeitsgruppe Teerschwele in Museumsdorf Düppel, Berlin, Germany), and two archaeological adhesives collected from glass *opus sectile* fragments found in the northern necropolis of Antinoopolis (Egypt, 4th–5th century AD) to establish a correlation with the mixtures obtained by experimental archaeology.

2. Materials and methods

2.1. Chemicals

All solvents were Carlo Erba (Milan, Italy) pesticide analysis grade. *n*-Hexadecane (internal standard, IS_1), tridecanoic acid, (internal standard, IS_2), hydrochloric acid (HCl), potassium hydroxide (KOH), and *N*,*O*-bis(trimethyl)silyltrifluoro-acetamide (BSTFA) containing 1% trimethylchlorosilane, were purchased from Sigma–Aldrich (Milan, Italy).

2.2. Samples

Following traditional procedures, reference pitch was obtained after two days of pyrolysis of pine wood (*P. sylvestris* L. Roots) according to the "Pile (autothermal)" process (carried out by Andreas Kurzweil, Arbeitsgruppe Teerschwele in Museumsdorf Düppel, Berlin, Germany). The pitch was produced using an autothermal method where resinous wood is piled in a wide pit covered in the centre with clay. The firewood heats the resinous wood from the upper part of the pile and inside the pile the temperature ranges from 400 to 700 °C [12]. Varying amounts of beeswax were added to the pine pitch after heating at 40–50 °C. Four mixtures with different proportions were thereby obtained with 10%, 33%, 50% and 70% (in weight) of beeswax, respectively.

The mixture of pitch from *P. sylvestris* L. and beeswax ("Zopissa"), whose relative proportions were unknown, was prepared by Andreas Kurzweil (Arbeitsgruppe Teerschwele in Museumsdorf Düppel, Berlin, Germany). Two archaeological adhesives (Samples 2 and 3) collected from glass *opus sectile* fragments found at the northern necropolis of Antinoopolis (Egypt, 4th–5th century AD), whose chemical composition (mixture of pine pitch and beeswax) was already obtained by GC/MS [15], were also used in this study.

2.3. DSC

DSC measurements were performed by a Perkin Elmer Pyris Diamond Differential Scanning Calorimeter in the temperature range 10–550 °C, with a heating rate of 10 °C/min and using air as purging gas. The sample masses of about 3 mg were prepared in aluminium pans.

2.4. TG-FTIR

Thermogravimetric (TG) analysis were performed using a TA Instruments Thermobalance model Q5000IR equipped with an FT-IR Agilent Technologies spectrophotometer model Cary 640 for Evolved Gas Analysis (EGA). TG measurements were performed at a rate of 10 °C/min, from 50 °C to 600 °C under air and nitrogen flow (25 mL/min). TG-FTIR measurements were performed at a rate of 20 °C/min, from 50 °C to 600 °C under nitrogen flow (90 mL/min), from 600 to 3000 cm^{-1} with a slit (4 cm^{-1} in width). To reduce the strong background absorption from water and carbon dioxide in the atmosphere, the optical bench was usually purged with nitrogen. In additional, a background spectrum was taken before the beginning of each analysis in order to zero the signal in the gas cell and to eliminate any contribution from ambient water and carbon dioxide. The amount of sample in each TG and TG-FTIR measurement varied between 2.4 and 3.8 mg.

2.5. GC/MS

Sample (1–3 mg) was subjected to alkaline hydrolysis by adding 1 mL of methanolic KOH (KOH in CH_3OH (10 wt%)/KOH in H_2O (10 wt%), 2:3), and heating at 60 °C for 3 h. After hydrolysis, neutral organic components were extracted with *n*-hexane (3 × 500 μL) and, after acidification with hydrochloric acid (10 M; to pH 2), the acidic organic components were extracted with diethyl ether (3 × 500 μL). Aliquots of both fractions were evaporated to dryness under a gentle stream of nitrogen and subjected to trimethylsilylation. This was achieved by mixing the dried aliquots with an internal standard solution (5 μL of tridecanoic acid solution, 140 μg/g) and derivatising with 20 μL of BSTFA (at 60 °C, 30 min), using 150 μL isooctane as the solvent. After adding 10 μL of *n*-hexadecane solution (80 μg/g) as an internal standard for the injection, 2 μL of the solution were analyzed by GC/MS.

The Gas Chromatograph System 6890 N (Agilent Technologies, Palo Alto, CA, USA) was coupled with a 5973 Mass Selective Detector (Agilent Technologies, Palo Alto, CA, USA) single-quadrupole mass spectrometer. For the gas chromatographic separation, an HP-5MS fused silica capillary column (5% diphenyl-95% dimethyl-polysiloxane, 30 m × 0.25 mm i.d., J&W Scientific Agilent Technologies, USA) with a de-activated silica pre-column (2 m × 0.32 mm i.d., J&W Scientific Agilent Technologies, USA) was used.

The split-splitless injector was used in splitless mode at 320 °C. The GC/MS parameters for the analysis of the various fractions were as follows: 80 °C isothermal for 2 min, 10 °C/min up 200 °C and