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Evidence concerning oxidation as a surface reaction in Baltic amber

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ABSTRACT

The aim of this study was to provide evidence about oxidation as a surface reaction during degradation of Baltic amber. A clear understanding of the amber–oxygen interaction modalities is essential to develop conservation techniques for museum collections of amber objects. Pellet-shaped samples, obtained from pressed amber powder, were subjected to accelerated thermal ageing. Cross-sections of the pellets were analyzed by infrared micro-spectroscopy, in order to identify and quantify changes in chemical properties. The experimental results showed strong oxidation exclusively at the exterior part of cross-sections from samples subjected to long-term thermal ageing, confirming that oxidation of Baltic amber starts from the surface.

1. Introduction

The aim of this research was to provide evidence about oxidation as a surface phenomenon during degradation of Baltic amber.

The role of oxygen in the degradation process of Baltic amber is still the subject of studies. A deep understanding of the amber–oxygen interaction modalities is essential for the comprehension of degradation processes and for the development of both active, i.e., based on the application of polymeric coatings, and preventive, i.e., based on the control of environmental parameters, conservation techniques for museum collections of amber objects.

One of the major chemical degradation mechanisms in Baltic amber is oxidation of diterpenoid components (labdanoid diterpenes, i.e., communic acid, communol and succinate ester [1,2]), where unsaturated carbon–carbon bonds are oxidized to acid groups [3,4]. Oxidation is thought to be a surface reaction due to the low porosity of the material and the resulting slow diffusion of gases through it [5], but new experiments were necessary to provide evidence.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy has previously been used on Baltic amber to identify and quantify oxidation through changes in surface chemical properties [5–7], but never to investigate bulk properties.

In the present study, pellets were produced from pressed amber powder and were used as test material because of the excellent repeatability and the optimal signal to noise ratio on ATR-FTIR spectroscopic analyses. Successively, micro-ATR-FTIR spectroscopy was applied on cross-sections produced from both unaged and thermally aged amber pellets, in order to obtain information about the development of oxidation in relation to the distance from the external surface.

2. Materials and methods

A large piece of raw Baltic amber (approximately 15 cm × 12 cm × 6 cm) from Rav Fehrn ApS (Søborg, Denmark) was selected for its visible homogeneity, uniform translucency and colour, together with the absence of sedimentary matrix on the external surface as well as organic/inorganic inclusions.

In order to prepare the pellets, specific procedures were used to limit any additional degradation effects due to the formation of free radicals [8] and to minimise the presence of pores, which might influence the diffusion of gases through the material. The authors of the present report describe these procedures in details in a previous work [6]. In total nine 2 mm-thick amber pellets were prepared.

Three pellets (group A) were kept unaged, each one of the remaining six (three in the group B and three in the group C) was placed in a glass Petri dish and subjected to accelerated thermal ageing at a temperature of 70 ± 2 °C, in the absence of light, in a Memmert UL 50 oven, for 35 days (group B) or 70 days (group C).

During the analysis, each pellet was cut along the diameter in two equal parts, using a Buehler Isomet low speed electrical saw,

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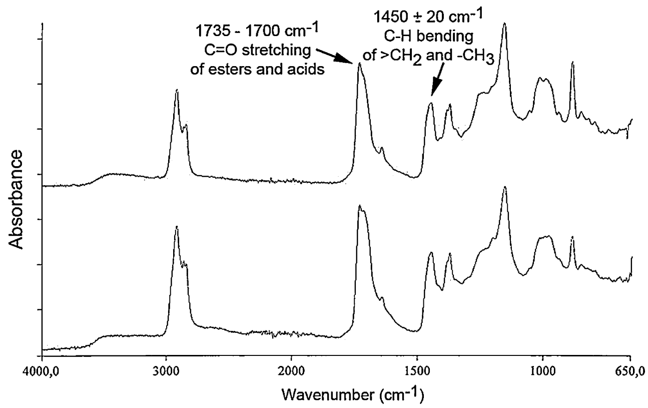

Fig. 1. ATR-FTIR spectra of unaged (top) and thermally aged (bottom) Baltic amber. The infrared bands used to quantify oxidation levels of the amber pellets cross-sections are indicated. The negative slope of the shoulder at 1250–1175 cm^{-1} and the decrease in intensity of the band at 888 cm^{-1} due to oxidation are also evident in the aged amber spectrum.

cooled with a water solution (3%) of additive for cooling fluid without amine compounds from Struers A/S (Ballerup, Denmark). Pellet cross-sections were washed with deionized water before each analytical measurement in order to remove any additive residues.

The ATR-FTIR spectra were collected using a Perkin Elmer AutoImage FTIR microscope equipped with an ATR diamond/ZnSe reflection element, a liquid nitrogen cooled mercury cadmium telluride (MCT) photoconductive detector and the programme Perkin Elmer Spectrum version 6.2.0 + AutoImage.

Absorbance spectra were acquired over the range of 4000 cm^{-1} and 650 cm^{-1}, with 50 scans at a resolution of 8 cm^{-1} and through a measuring field of 100 μm × 100 μm; background spectra were run at hourly intervals.

Each cross-section was placed under the microscope objective-ATR crystal and analyzed. Spectra related to 15 points on the cross-section (three random points at five different levels between the external surface and the core) were collected and the absorbance value of each level was calculated as average of three measurements.

The method developed to quantify levels of oxidation of the amber samples by ATR-FTIR during the accelerated ageing was based on the same method previously used by the authors of this work in other studies [6,7] (Fig. 1).

3. Theory

Micro-ATR-FTIR analysis of amber pellets cross-sections was performed in order to obtain information about the development of oxidation along the section. The data obtained from the measurements were analyzed through both critical evaluation and simple statistical tests, e.g., *t*-test for paired data.

Fig. 2 presents a plot of the changes in the carbonyl group concentration versus distance from the surface.

Shashoua et al. propose oxidation of amber as a surface reaction because of the low permeability to oxygen of the material [5]. This work confirmed that oxygen reacts first with the surface, as showed by micro-ATR-FTIR spectroscopy results.

The detected levels of oxidation showed no significant difference between unaged and 35 days-aged samples. In samples that were aged for 70 days, the strong increase of oxidation at the exterior part was clearly visible, suggesting that oxidation of amber occurs initially only at the surface. Although it is not clear why there was an induction period for oxidation, reaction of oxygen with

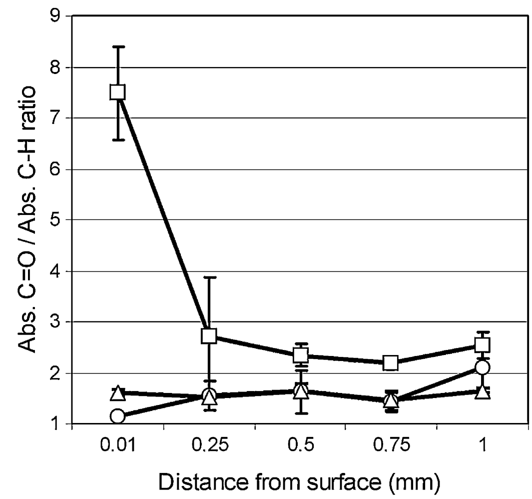

Fig. 2. C═O group concentration changes at different levels in unaged and aged amber pellets cross-sections. Key to the symbols: ○ – group A (unaged), △ – group B (aged for 35 days), □ – group C (aged for 70 days). Error bars represent standard errors.

unsaturated carbon–carbon bonds in the terpenoid components present at the surface likely resulted in the formation of carboxylic acids.

Consequently, the ideal conditions to obtain a good preservation of Baltic amber objects could include both active and preventive techniques to limit surface oxidation. Because polymeric coatings on amber should be avoided [4,9], a more effective inhibitive approach would be appreciated, for instance using oxygen free cases during storage, transport and display of museum collections of amber objects.

Micro-ATR-FTIR spectroscopy proved itself as a valuable method to locate and quantify oxidation of Baltic amber, allowing further studies to better characterise the observed induction period, to obtain clearer details on the oxidation profile and, in general, to enhance the understanding of chemical mechanisms involved in the degradation of museum amber objects.

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