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Case study

Accelerated ageing of cotton canvas as a model for further consolidation practices

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ABSTRACT

In order to assess the effectiveness of various practices for canvas consolidation, model substrates are needed. In this work, a method of rapid ageing of cotton canvas is described. The method consists of treatment of the canvas with a mixture of hydrogen peroxide and sulfuric acid at 40 °C during 72 hours to mimic to some extent the natural processes of oxidation and acid-catalysed hydrolysis of cellulose. Two protocols for canvas degradation were developed, which reduced the degree of polymerization of cellulose from *ca.* 6250 to *ca.* 1350 and 450. The reduction of the mechanical properties and the increase of the negative charge were also quantified. These samples were compared with a canvas degraded using a state-of-the-art method that takes up to 20 days. The results show that the developed method can provide a rapid procedure for preparing small samples for testing various consolidation strategies by conservators.

1. Introduction

An important problem with easel painting conservation is to arrest the degradation process occurring with its organic components, one of which is cellulosic canvas, and to consolidate the degraded material. The degradation process results in deterioration of the canvas strength and ultimately affects the integrity of the paint layer. When the canvas is subjected to tension on a stretcher, the degradation is influenced by various parameters: humidity and temperature fluctuations, UV irradiation, chemistry of different painting layers, air pollution, etc. [1–3]. Undoubtedly, it is hard to determine the exact influence of all these parameters (separately or together) on the canvas properties in the long-term perspective. However, it is generally known that the two dominant processes involved in cellulose degradation are oxidation and acid-catalysed hydrolysis [4–7], as shown in Fig. 1.

Cellulose oxidation originates, for instance, from acidic gases, such as nitrogen dioxide (see Fig. 1a). Additionally, photo-oxidation and thermal oxidation occur that involve light absorption by certain substances, e.g., pigments, varnish or lignin, which create free radicals that initiate the oxidation process [6,7]. As a result, hydroxyl groups of cellulose chains are converted to carboxyl groups that have an acidic character [8].

The presence of acid catalyses the hydrolysis reaction that leads to scission of cellulose chains, transforming acetals to hemiacetals (see Fig. 1b). The cellulose chains are packed together forming nanofibrils that in turn are arranged to compose a cell wall of a single microscopic fibre [9]. The acid-catalyzed hydrolysis leads to a drastic decrease of the degree of polymerisation (DP), i.e., reduction of the length of the polymeric chains, which can be correlated to a reduction of the mechanical strength of the fibres [2]. For instance, for cotton the DP varies in the range of 8000–14,000 depending on the treatment of the raw material [10]. During the degradation process, the DP is drastically decreased. It has been reported that a cotton painting canvas in satisfactory condition has a DP of *ca.* 1000, whereas a canvas with a DP of < 600 is referred to as "very fragile", i.e., a painting with a canvas with such a low DP will have a high risk of being torn when handled [2]. The correlation between canvas degradation and its mechanical properties has been presented in a number of papers [11–13].

Various conservation practices are available for consolidation of degraded canvases [14–17]. Therefore, model substrates are needed by conservators in order to assess the effectiveness of different practices and some previous works have focused on accelerated

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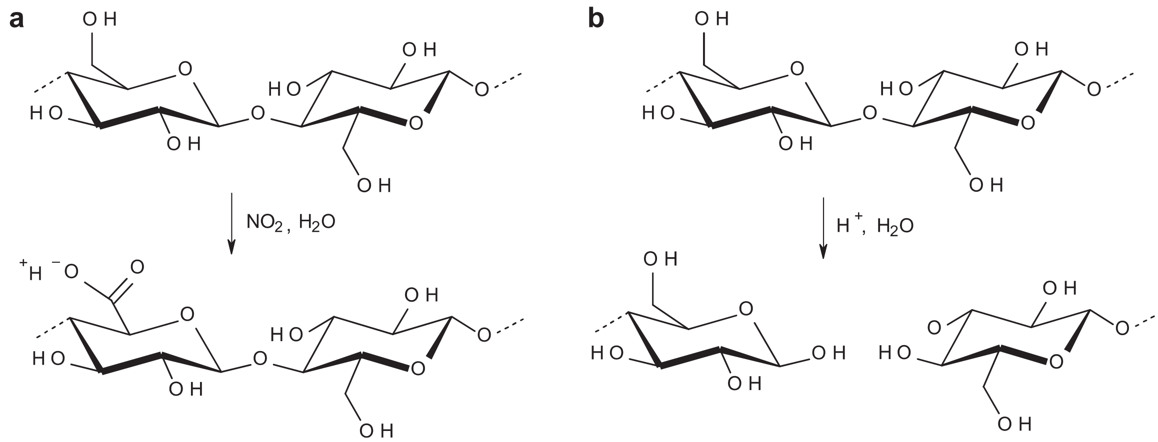

Fig. 1. Degradation mechanisms of cellulose chains: (**a**) oxidation of hydroxyl groups yielding carboxylic acids (in this case nitrogen dioxide, a well-known atmospheric pollutant, acts as oxidant) and (**b**) acid-catalysed hydrolysis leading to cleavage of the polymeric chains.

ageing of cellulosic canvases [5,18–20]. It is known that cellulose can be degraded by various treatments, e.g., thermal, hydrolytic, photolytic, photochemical and enzymatic [11]. Hackney and Hedley [5] used light exposure for accelerated aging tests of linen canvas. Seves et al. [18] studied the accelerated thermal ageing of linen canvas. Carr et al. [19] used sulphuric acid treatments of linen canvas. Poggi et al. [20] reported a method of canvas ageing by soaking in sulfuric acid followed by thermal degradation. These methods offer possibilities to artificially degrade the canvas; however, they are all time consuming. For instance, the method of Carr et al. was carried out during 500 hours and the one of Poggi et al. for up to 300 hours.

In this work, a method of accelerated ageing of cotton canvas, which takes only 72 hours and which uses a mixture of hydrogen peroxide and sulfuric acid, is described. We focus on cotton since it represents the pure natural form of cellulose, compared to other natural fibers that contain lignin. Cellulose is the main component responsible for fiber strength and its degradation directly influences the reduction of the mechanical properties of the canvas. Therefore, cotton was used in this study. Another reason to choose cotton is the lack of methodologies for this type of canvas material. Cotton has been widely employed as canvas material in contemporary art due to its intrinsic properties (white colour) and more favourable price compared to linen, which has been most commonly used due to its superior mechanical properties [21,22].

2. Research aim

The aim of this work is to develop a rapid procedure to prepare a material that resembles the naturally aged painting canvas (subjected to usual storage conditions of paintings with respect to humidity, temperature and UV level) in terms of:

- mechanical properties;
- DP;
- charge density (a measure of charge per unit of mass);
- chemistry.

These data are difficult to find for naturally aged canvases, since the treatment and the handling history are usually unknown, leading to a broad spectrum of properties, not necessarily attributed to the degradation process of cotton. Therefore, in scope of this study, we target the other methodology of artificial ageing, reported by Poggi et al. [20], as a benchmark. This rapid degradation is aimed as a method to produce a model canvas that can be used for evaluation of the efficiency of various consolidation practices.

3. Materials and methods

3.1. Materials

The cotton canvas with a basis weight of 417 ± 3 g/m^2 and a plain weave was purchased from Barna Art (Barcelona, Spain). Hydrogen peroxide solution (35 wt%) was purchased from Fisher Scientific GTF AB, Sweden. Sulfuric acid (95–97 wt%) was purchased from Merck Chemicals and Life Science AB, Sweden.

3.2. Canvas preparation

The canvas was washed prior to the measurements (DP, charge density, tensile testing, etc.) in order to remove residues of grease (e.g., tallow or mineral oil), commonly used in fabric weaving processes [23,24], as well as possible sizing agents, both of which impart hydrophobicity to cellulose. The canvas (*ca.* 1 m^2) was washed in a domestic washing machine at 60 °C for *ca.* 40 min without any detergent and then kept in water in a 1 L double-jacket reactor at 85 °C with mechanical stirring. The washing was not performed prior to the accelerated ageing, which itself was very efficient for removal of the hydrophobic impurities.

3.3. Accelerated ageing

3.3.1. Moderately degraded (MD) and highly degraded (HD) canvases

Two models of aged canvas were developed by accelerated degradation. The method consists of treatment of 70 × 80 mm new cotton canvas specimens (1.78 g) in a mixture of 200 mL of hydrogen peroxide (H_2O_2) solution (35 wt%) and either 10 or 1 mL of sulfuric acid (H_2SO_4), resulting in models of highly degraded (HD) and moderately degraded (MD) canvas, respectively. The treatment was performed during 72 hours at 40 °C with mild magnetic stirring in the setup shown in Fig. 2. The magnetic bar was placed in a beaker and covered with a pierced polystyrene cup in order to avoid contact between the bar and the canvas, located above. The canvas was pressed with a polytetrafluoroethylene brick to avoid floating. After the ageing reaction, the canvas was thoroughly washed with deionized water until the conductivity of the effluent was < 5 μS/cm and was then dried under biaxial tension to prevent shrinkage.

3.3.2. State-of-the-art degraded (SAD) canvases

The above method was compared with a state-of-the-art degradation (SAD) method using sulfuric acid and thermal degradation, reported by Poggi et al. [20]. The method was performed with some