



Characterization and degradation of poly(vinyl acetate)-based adhesives for canvas paintings



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ARTICLE INFO

Article history:

Received 29 August 2013

Received in revised form

30 October 2013

Accepted 23 December 2013

Available online 2 January 2014

Keywords:

Polyvinyl acetate

Acrylate

Adhesives

Accelerated degradation

Thermal analysis

Canvas painting

ABSTRACT

The modifications occurring to two well-established synthetic formulations (Mowilith DMC2[®], Mowilith DM5[®]), upon accelerated degradation, were investigated. Degraded films of copolymers were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Differential Thermogravimetry (DTG), Atomic Force Microscopy (AFM) and colorimetry. The study highlighted the varied degradation of the two adhesives, which exhibit yellowing, alteration of their thermal and spectroscopic features and changes in their surface morphology and viscoelasticity. The main degradation route is characterized by the loss of acetyl groups, resulting in conjugated double bonds, as suggested by colorimetry and confirmed by FTIR. The loss of volatile organic acids represents a conservation issue when these adhesives are used for the lining of canvas paintings, since acidity promotes the hydrolysis of canvas cellulose. Rearrangement of the adhesives' molecular structure, and a competition between depolymerization and cross-linking were suggested by AFM and thermal analyses (changes in molecular weight are known to affect the solubility of copolymers and the possibility of their removal from works of art). The representativeness of the accelerated degradation protocol was positively assessed through comparison with naturally degraded adhesives.

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1. Introduction

Lining is a fundamental technique for the restoration of canvas paintings and it has been widely used since the 17th century. The technique consists in re-adhering the painted layer and in strengthening the original canvas through the application of a new support canvas, glued on the back of the painting [1]. Many different formulations have been used in the past for the preparation of natural glues [2]. In the second half of the 20th century, research on synthetic adhesives opened up new possibilities to restorers, who adopted vinyl acetate and acrylate copolymers, also due to their decreased sensitivity to relative humidity and visible or ultraviolet light. Polyvinyl acetate latexes prepared with polyvinyl alcohol (emulsifier) have been widely used as adhesives, and vinyl acetate is copolymerized with different monomers such as

ethylene, dibutyl maleate and others [3]. However, acrylates and vinyl polymers can undergo several degradation processes that eventually result in discoloration, loss of adhesive power, and emission of organic acids that cause cellulose hydrolysis and oxidation processes [4–6]. Given the large extent to which lining is carried out in painting restoration, and owing to the growing social and economic impact of cultural heritage conservation, it is important to characterize the degradation of synthetic commercial products used in past and present restoration interventions.

The literature reports many studies on the thermal and photo-degradation of acrylates and vinyl polymers [7–13]. It is known that the thermal degradation of polyvinyl acetate (PVAc) in extreme conditions (temperatures between 190 and 300 °C) results mainly in the formation of acetic acid; the process is non-radical and has an autocatalytic character (except for the initiation step), and the mechanism involves random initiation and gradual zip propagation [12,13]. Both the pre-exponential factor and the activation energy for the random elimination of acid increase with the molecular weight of the polymer if $M_n < 10^5$, and for zip propagation these parameters probably depend on the morphology of the polymer chain [12]. Deacetylation is followed

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by disintegration of the polyolefinic backbone around 440 °C [11]. A recent study by Toja et al. investigated the influence of mild thermal-oxidative degradation ($T = 60$ °C) on both standard and plasticized PVAc films comparing the results with those obtained through photo-oxidative degradation simulating exposure to sunlight [9]. The authors found that for standard PVAc thermal degradation enhanced the formation of C=C bonds along the polymer backbone, and plasticized films showed a rapid decrease in the additive (dibutyl phthalate) content. Both acid evolution and the loss of plasticizers alter the mechanical and chemical properties of PVAc, causing brittleness, loss of tensile strength and darkening [14].

It must be noticed that strong photo-oxidative conditions are not representative of the natural degradation of lining adhesives, which lie between the original and the support canvas on the back of the painting, and are usually exposed to temperature and relative humidity oscillations, rather than light. Therefore, the aim of the present work was to investigate the accelerated hydrothermal degradation of two widely used synthetic adhesives (Mowilith[®] DM5 and DMC2) in order to reproduce degradation in natural conditions. This is fundamental to understand how the degradation of the adhesives affects the canvas supports, and if alteration of the products might change their solubility in solvents. Moreover, it was important to highlight the different behavior of the two adhesives, which have often been applied as a mixture for a wide number of restoration purposes besides canvas lining, including consolidation of wall painting, wood, paper or metal.

Pre- and post-degradation characterization was performed through Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Differential Thermogravimetry (DTG), Atomic Force Microscope (AFM) and colorimetry. Finally, real samples of adhesives, coming from naturally aged works of art, have been characterized as reference materials, in order to state the representativeness of the accelerated degradation protocol.

2. Materials and methods

2.1. Materials

Mowilith[®] DMC2 is a copolymer of vinyl acetate (65%) and dibutyl maleate (35%) in aqueous emulsion. Dibutyl maleate is used as an internal plasticizer. According to the literature, other compounds can be present, e.g. cellulose ether and surfactants [15]. The broad band between 3140 and 3700 cm^{-1} (OH stretching) in the FTIR spectrum of the DMC2 sample (see Fig. 1a) could be ascribed to cellulose ether additives or to the presence of polyvinyl alcohol. No band could be ascribed specifically to the presence of surfactants, probably due to the low concentration of these additives and to overlap with the copolymer bands [16].

Mowilith[®] DM5 is a copolymer of vinyl acetate (65%) and *n*-butyl acrylate (35%) in aqueous emulsion. The acrylate is used as an internal plasticizer.

In restoration practice Mowilith DM5 has been often mixed with Mowilith DMC2 to decrease the temperature of softening. For instance, the heat-sealing temperature of Mowilith DMC2 is 60–80 °C but can be decreased depending on the proportion of Mowilith DM5 added [17]. Films of Mowilith DM5 are softer and more rubbery than films of Mowilith DMC2, which are tougher and harder [17].

For this study, films of Mowilith DM5 and DMC2 were laid on glass slides and let dry before being characterized and degraded. Film thickness was ca. 75 μm .

Two real samples of PVAc-based adhesives (mixed with “colle de p \hat{a} te” glue), coming from the back of naturally aged lined canvas,

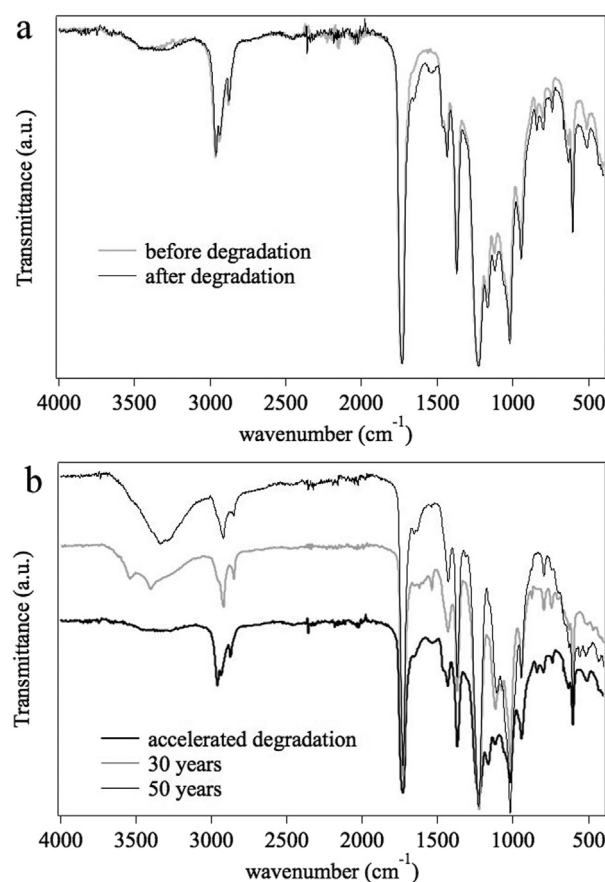


Fig. 1. FTIR spectra of: (a) Mowilith DMC2 films before and after accelerated degradation; (b) a polyvinyl acetate adhesive that underwent 30 years of natural degradation, of a polyvinyl acetate adhesive that underwent 50 years of natural degradation, and of a Mowilith DMC2 film after 9 cycles of accelerated degradation.

were chosen as reference materials. The “colle de p \hat{a} te” (“paste glue”) is a mix of flour glue, rye glue, rabbit-skin glue, turpentine (as internal plasticizer) and phenol (as biocide), and is a classic lining adhesive that has been used for centuries. The first real sample came from the back of a painting lined in the 1970s, belonging to a private collection. It underwent natural degradation for 30 years under strong relative humidity (RH) and temperature variations. The second sample came from the back of a lined canvas that underwent 50 years of natural degradation inside a church with no hydrothermal regulation. The “colle de p \hat{a} te” content varied between 10 and 20%.

2.2. Accelerated degradation

A protocol for the accelerated degradation of samples was developed by modifying degradation cycles already used by Berger and Zeliger for the testing of Beva 371, a thermosetting adhesive based on ethylene vinyl acetate, used in canvas lining [18]. Our purpose was to simulate and accelerate, in the most representative way, the degradation conditions that adhesives commonly experience when lined canvas paintings are stored and exposed in ateliers, private houses, castle halls and indoor environments where temperature and RH are not controlled. PVAc has a certain hydrophilicity, and the adsorbed humidity acts as a plasticizer lowering the polymer glass transition temperature [19,20]. Moreover, PVAc is sensitive to hydrolysis in acidic (or basic) media to give polyvinyl alcohol [20].

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