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Durability of an industrial epoxy vinyl ester resin used for the fabrication of a contemporary art sculpture

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ABSTRACT

In this study we report on an assessment of the conservation condition of a sculpture partially made of synthetic polymers, and on the prediction of its long term durability. Compositional analysis, largely based on IR spectroscopy and Raman spectrometry, identified the epoxy vinyl ester resin used for modelling the lower part of the sculpture as the most critical component. Accelerated degradation tests of the epoxy vinyl ester resin possibly employed by the artist were performed in a photodegradation device and separately in a forced-air circulation oven at 140 °C, to simulate natural degradation. The results obtained by monitoring structural and molecular changes by FTIR and UV–Vis spectroscopy, thermogravimetry (TGA) and differential scanning calorimetry (DSC) allowed us to propose a comprehensive mechanism of oxidation. The validity of the prediction of the durability of the resin was corroborated through a comparison with the results obtained evaluating the actual state of conservation of the artwork.

1. Introduction

Plastics and, by extension, synthetic polymers have been used by artists for the fabrication of their artworks since the period between the two world wars but it was only after the second World War and later in the 50s and 60s that synthetic polymers, omnipresent in our daily lives, became a reference material not only for painters but also for the creation of sculptures [1]. Commercial materials were usually selected without taking into account that they were developed for applications and purposes far different from those considered essential from an artistic point of view, where aesthetic rendering and the expansion of the forms of expression are much more important than other aspects such as the durability of the artwork. Artists moved from established traditional materials to little known, and frequently unknown, synthetic polymers, intrinsically much more prone to interact with the environment and sometimes prone to deterioration faster than had been expected [2].

The interest in issues relating to the durability of modern and contemporary artworks, especially sculptures, completely or partially realized in synthetic polymers is rather recent. In fact, only in the last two decades have museums, conservators and material scientists focused their efforts on the evaluation of the actual state of conservation and on the study of the degradation of the constituent materials, with the aim of predicting their evolution and producing conservation and management strategies for collections [3,4]. In many cases, the state of conservation of this specific class of sculptures is as critical as that of older plastic artefacts found in collections and museums devoted to science and technology, modern history and design, etc., which have recently drawn attention. As examples, it is worth citing specific investigations on the durability of cellulose nitrate and acetate artefacts [5,6], poly(vinyl chloride) objects [7], polyurethane foams in fashion and upholstery [8] and poly(vinyl acetate) in design objects [9,10], or, more generally, on plastic objects' conservation [11,12] and management in museums [13]. The fact that polymers in contemporary art sculptures often face serious degradation problems, either consisting of simple color changes, small increases in brittleness or more serious structural failure, even in protected indoor environments during display and storage may be due to the following two main reasons:

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- selection by the artist of polymers developed for short-, or medium-term household and industrial applications, e.g. materials for packaging and single-use objects, or for applications in which shading or eventual color changing are not critical, such as for some thermosetting resins and in composite materials, or in foams used for cushioning, etc.;
- inappropriate manipulation or preparation of the polymer, especially in the case of thermosetting resins or composites, or in the formulation of multicomponent materials, which introduce unexpected and unpredictable untimely degradation.

Several examples of critical issues concerning the inappropriate use of synthetic polymers have been reported in the last years, usually focused on the deterioration of specific artworks, considered as case studies, and focused on industrial polymers, e.g. polyisoprene [4], unsaturated polyesters [14–16], epoxy resins [4,17], poly(ether urethane) elastomers [4] or expanded polystyrene [18]. In addition, a few comprehensive investigations on the degradation behavior of specific polymers of common use by contemporary artists, such as polyurethane foams [19,20], and polyamides [21–23] may also be found.

In the framework of a comprehensive project aimed to develop a multi-analytical approach for evaluating the degradability of polymeric materials in contemporary works of art [4], herein we focus our efforts on the evaluation of the actual state of conservation and the prediction of the long term stability of a sculpture (*Nemeas Lion* by *F. Leiro*) partially modeled with an unknown resin. After identification of the constituent materials by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and Raman spectrometry, the critical component which constitutes the more degradable interface with the environment, which was found to be an epoxy vinyl ester resin, was investigated under accelerated degradation conditions in which the processes occurring under natural conditions were accelerated by either an isothermal treatment or through irradiation in a photodegradation device. A study of the degradation behavior of a specific commercial resin, reasonably similar to the one used by the artist, was necessary due to the relatively large structural variability of commercially available products which made the amount of data published on this class of resins useful only as reference literature, mostly focused on curing [24,25] or on the degradation of different systems [26–29]. In particular, it was reported that for the case of an epoxy vinyl ester network based on bisphenol A UV irradiation leads to the formation of degradation products with low molecular weight and high volatility, saturated ester functions and polyhydroxy ether structures, together with CO and CO_2 elimination [27].

The effects of degradation on reference samples were monitored not only by typical instrumental techniques for polymer characterization, essentially FTIR and UV–Vis spectroscopy, thermogravimetry (TGA) and differential scanning calorimetry (DSC), but also through non-instrumental measurements, such as visual inspection and weight loss determination.

2. Experimental

2.1. Reference resin

The reference epoxy vinyl ester resin components were supplied by Ashland Spain and the resin network prepared as indicated in the technical data sheets. The epoxy vinyl ester resin Derakane® Momentum 411-350 was mixed with 1.5% of methyl ethyl ketone peroxide Norox® MEKP-925H and left for 24 h at 20 °C. Curing was completed by heating the samples as films at 120 °C for 2 h.

2.2. Degradation treatments

The samples for degradation treatments were prepared in the form of thin films with a thickness of less than 100 μm. Film thickness was deduced from the amount of solution used for the preparation considering a uniform deposition. Samples for UV–Vis spectroscopy were supported on quartz windows, whereas for all other determinations they were prepared onto 76 × 26 mm glass slides. Accelerated photodegradation was carried out in a high-speed exposure unit Suntest CPS (Heraus), equipped with a xenon light source having a constant irradiation at a power of 765 W/m^2; a glass filter with cutoff at $\lambda \leq 295$ nm was used to exclude radiation more energetic than that of outdoor solar exposure. The maximum temperature of the samples during irradiation was 45 °C black panel temperature. Accelerated degradation was also performed by accelerating the natural process of degradation in a forced-air circulation oven, maintained at a constant temperature. Thermally accelerated degradation treatments were carried out at 140 °C. All the degradation tests were performed in triplicate.

2.3. Characterization techniques

Weight losses of polymer films induced by degradation were determined gravimetrically whereas their surface changes were monitored by a Bresser USB digital microscope at 20× and 100× magnifications; in order to compare color changes, pictures were taken under identical lighting conditions and without flash, using a digital camera. FTIR absorption spectra in ATR mode were collected with a Thermo Nicolet FT-IR Nexus instrument equipped with a Smart Endurance device, and a DTGS detector, at a 4 cm^{-1} resolution for 128 scans. Spectroscopic acquisitions and data treatments were performed using Omnic v. 6.1 (Thermo Nicolet). FT-Raman spectra were recorded in the region 200-3500 cm^{-1} on a Bruker IFS 66 optical bench with an FRA 106 Raman module attachment. The excitation source was a 1064 nm near-infrared Nd-YAG laser with a nominal power of 100 mW. The scattered light was filtered and collected on a liquid nitrogen cooled germanium-diode detector giving a resolution of approx. 0.2 cm^{-1} between individual pixels. Spectra in the UV and visible region were measured from thin films onto quartz windows with a diode array Hewlett–Packard HP8452 spectrophotometer.

DSC analyses were carried out under nitrogen flow with a Q200 Differential Scanning Calorimeter (TA Instruments), with a scanning rate of 20 °C/min. Sealed aluminum pans containing ca. 10 mg of sample were used. Finally, TGA measurements were performed with a Q5000 IR thermobalance (TA Instruments), operating under nitrogen flow, at a scanning rate of 20 °C/min. Thermal characterization measurements were performed in triplicate on samples collected from different thin films.

3. Results and discussion

3.1. Compositional analysis

In contrast to the case of old artworks where the use of non-destructive analytical techniques is almost compulsory, contemporary works of art and especially sculptures may sometime be investigated by microdestructive techniques, as fragments weighting several milligrams can, as in the present case, be available. Samples in form of debris could be collected from the storage cases of the sculpture visible in Fig. 1, created by Francisco Leiro in 1995 and part of the collection of the contemporary art museum of Santiago de Compostela. In addition, smaller fragments were collected from selected areas during cleaning treatments.