

The degradation of poly(vinyl acetate) as a material for design objects: A multi-analytical study of the effect of dibutyl phthalate plasticizer. Part 1

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ABSTRACT

The influence of dibutyl phthalate (DBP) plasticizer on poly(vinyl acetate) (PVAc) degradation was investigated. A multi-analytical approach (combining FTIR and Fluorescence spectroscopy, NMR and DSC analyses) was used to study how thermal- and photo-oxidative ageing treatments act on the polymer and assess the role of the additive in the degradation pattern. Standard and plasticized PVAc films were artificially aged at 60 °C in a thermal regime and irradiated at wavelengths above 290 nm in a photo-oxidative ageing regime, with exposure between 100 and 2000 h. The two types of ageing differ mainly in the formation of C=C double bonds along the polymer backbone, enhanced by thermal ageing, and the formation of aldehydic structures, following photo-oxidative treatment and in the degree to which plasticizer is lost. The integration of results from different analytical methods highlights the utility in combining complementary analyses for the study of PVAc degradation.

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1. Introduction

Plastic compounding is a fundamental process since polymers require chemical modifications to optimize their chemical and physical properties which include resistance to surfactants, strain, high temperatures, oxidation, impact, and ultraviolet radiation. Therefore, plastics are available in a wide range of formulations where base polymers are mixed with both organic and inorganic materials which include additives, metal powders and glass fibers [1]. Additives are fundamental components which provide stability to polymers, ensuring good mechanical properties, performance and long-term use and can prevent or delay degradation of the composite plastic formulation [2,3]. Each additive has a different effect on the properties and the ageing of materials and can play a key role in the success or structural failure and chemical degradation of objects in plastic [4,5]. It is well known that additives highly influence the pattern of degradation because of their loss,

evaporation and migration to the surface, and also due to their reactivity with environmental agents [6–8].

The assessment of the role of additives in polymers degradation is a critical aspect for the conservation and preservation of artefacts made in plastic. In fact, polymers are increasingly used to create artworks, and objects partially or completely made of plastics may be found in international collections [9]. Cellulose-based materials, plasticized PVC, polyether-based polyurethanes as well as polyvinyl esters are among the most widely used materials in this field. Nevertheless, plastics have shorter lifetimes than traditional materials (for example wood) because polymers, due to their nature, are much more susceptible to chemical degradation reactions [10]. Because of excessive exposure to light, heat, moisture, chemicals and gaseous pollutants, objects made in plastics may degrade very quickly and, in some cases, may have a useful lifetime of only a few decades [11].

In order to find effective ways to preserve these objects, conservation scientists need to carry out systematic studies with artificial or accelerated ageing [12]. Accelerated ageing tests are important to verify in an accessibly short time the relative chemical and physical stability of materials in museum-type conditions [13].

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In particular, mild ageing tests are suitable for modelling museum conditions and can be used to obtain results which are readily applicable to problems faced by conservators. However, it is difficult to predict the behaviour and durability of materials under normal conditions of use or exposure, based only on results obtained in hard accelerated-ageing tests. This paper presents a study on the effect of a widely used plasticizer, (DBP), on the degradation of poly(vinyl acetate) (PVAc) in mild, thermal- and photo-oxidative artificial ageing.

DBP is a colorless, odorless and viscous liquid usually used as a plasticizer in the chemical industry of elastomers, explosives and adhesives in concentrations between 1 and 20% [14–16] (Fig. 1a). It is widely used to plasticize poly(vinyl acetate) (PVAc) (Fig. 1b) emulsions and it is particularly appreciated for its chemical stability over irradiation and the lower volatility in comparison with shorter phthalates [17]. Thanks to these characteristics, DBP is an important component in PVAc formulations, as the additive enhances the durability of objects made of the polymer.

In extreme ageing conditions (at temperatures between 200 and 250 °C), it is known that acetic acid is the primary volatile product in the thermal degradation of PVAc [18]. The evolution of acetic acid is also favoured by UV irradiation. The degradation of PVAc occurs according to Norrish mechanisms [19–21] either with (a) hydrogen abstraction by an acyl radical followed by aldehyde formation, or (b) an intramolecular hydrogen abstraction and the formation of a double bond in the main chain as a consequence of the loss of an acetic acid molecule.

The degradation pattern of PVAc in mild conditions, for long periods of exposure, was recently investigated suggesting that main chain scission is the foremost photodegradation mechanism with a minimum formation of acetic acid [22,23]. Acid evolution, together with the loss of external plasticizers, leads to changes in the mechanical and chemical properties of PVAc and in particular an increased brittleness, loss of tensile strength, darkening, yellowing and loss of transparency [12]. Recently, the effect of mild UV ageing on a series of PVAc coatings, and the influence of pigment over degradation of the polymer has been investigated [23]; the irradiated material showed a high stability, with no gel formation reported after 5000 h of Xe-arch lamp irradiation. Moreover, metal ions present in the film did not seem to influence the photo-oxidative degradation pattern of the polymer, while chain scission is the principal degradation mechanism.

In the present work, PVAc was tested in thermal-oxidative ageing conditions at a temperature just above the second order transition temperature (60 °C) in the presence of oxygen [24]; in order to simulate photo-oxidative ageing due to the exposure to sunlight, a Xe solar lamp was used with a cut off filter at >290 nm. Polymer degradation has been assessed with a multi-analytical approach based on Fourier Transform Infrared (FTIR) spectroscopy, Fluorescence spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy and Differential Scanning Calorimetry (DSC).

2. Experimental

2.1. Materials

All reference reagents were purchased from Sigma Aldrich: poly(vinyl acetate), in beads (average $M_w \sim 100,000$); dibutyl phthalate (DBP) Reagent Plus[®], $\geq 99\%$; dichloromethane CHROMASOLV[®] Plus for HPLC $\geq 99.9\%$; chloroform-*d* 99.8 atom % D.

2.2. Instruments and methods

2.2.1. Preparation of plasticized polymeric films

PVAc films of approximately 80–100 μm thickness were prepared by solution casting of 20% wt. PVAc in dichloromethane, on glass microscopic slides (76 \times 26 mm). Films of PVAc with 10, 20, 30% wt. of DBP plasticizer were also prepared by solution casting in the same PVAc/dichloromethane solution. The films were dried at 60 °C for 2 h to ensure complete removal of the solvent, and then stored in a desiccator.

2.2.2. Thermal and photo-oxidative ageing treatments

Accelerated ageing tests have been conducted in two different regimes in oxygen:

- (1) Thermal-oxidative ageing was carried out over a 83-day period in an air circulating oven at a temperature of 60 ± 2 °C; the different samples were maintained in the oven for 100, 500, 1000, 1500 and 2000 h.
- (2) Photo-oxidative ageing was carried out in a Suntest CPS + chamber (Heraeus, Germany) equipped with a Xenon arc lamp source and a cut off filter for wavelengths below 290 nm; irradiation was kept constant at 765 W/m^2 and temperature was maintained at 51 ± 2 °C. Different samples were exposed to UV irradiation for 100, 500, 1000, 1500 and 2000 h.

2.2.3. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) analysis was carried out with a Nicolet 6700 spectrophotometer equipped with a DTGS detector. Spectra were recorded from solutions of PVAc deposited as films on NaCl windows in transmission mode in the optical bench between 4000 and 400 cm^{-1} with 64 acquisitions and 4 cm^{-1} resolution. The spectra were baseline corrected using Omnic software, and normalized based on the intensity of the CH_2 stretching vibration (2930 cm^{-1}), carbonyl symmetric stretching vibration (1740 cm^{-1}) or the $\text{CH}-\text{O}$ stretching vibration (1022 cm^{-1}).

2.2.4. Fluorescence excitation emission spectroscopy

Fluorescence spectroscopy of films of PVAc involved the acquisition of fluorescence excitation emission (EE) spectra with excitation between 250 and 500 nm and emission recorded between 280 and 750 nm. For this purpose, a Jobin-Yvon Fluorolog Spectrofluorimeter equipped with a 150W Xenon lamp, double excitation monochromators and a single emission monochromator, was employed for analysis of films in front face (23°) geometry. All measurements were acquired in the same conditions, and the glass substrates used for the preparation of PVAc films were analysed as blanks.

Slits were fixed to 1 nm for the excitation monochromators and 5 nm for the emission monochromator. Excitation, emission and synchronous fluorescence spectra (with an offset between the excitation and emission monochromators) were recorded for the different materials. In the text maxima in fluorescence bands are listed as excitation wavelength (nm)/emission wavelength (nm).

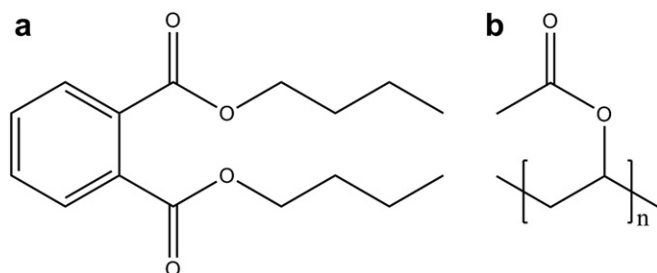


Fig. 1. (a) Dibutyl phthalate (DBP) and (b) poly(vinylacetate) (PVAc).

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