



Photodegradation of celluloid used in museum artifacts



Pierre-Olivier Bussiere^{a,b}, Jean-Luc Gardette^{a,c}, Sandrine Therias^{a,c,*}

^a Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France

^b Clermont Université, ENSCCF, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France

^c CNRS, UMR 6296, ICCF, BP 80026, F-63171 Aubière, France

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ABSTRACT

The consequences of the photodegradation of celluloid on the modification of the material properties have been analysed. Various techniques were used to follow the accelerated degradation provoked by exposure to light ($\lambda > 300$ nm). The objective was to relate the modification of the properties at various levels of investigation, from the molecular properties towards the degradation of the macroscopic properties. The modification of the chemical structure was followed by infrared and UV–visible spectroscopic analyses. Gloss and colour measurements were performed, as well as characterization of surface mechanical properties by microhardness and Atomic Force Microscopy (AFM). The results show that the loss of gloss and the decrease of the mechanical properties are a result of a combination of the progressive loss of plasticizer and chain-scission reactions. These developments were explained in light of the modifications of the chemical structure. Quantitative cross-correlations of the degradation chemistry with performance-critical physical properties were established.

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1. Introduction

Since the XIX^e century, artificial and synthetic polymers have been used to create features that became museum artifact collections and represent nowadays a non-negligible part of the cultural heritage exposed in museums. Celluloid was the first artificial and synthetic polymer up to 1900. Celluloid is based on cellulose nitrate (NC) mixed with camphor, used as plasticizer [1,2]. Celluloid was particularly popular as an imitation substitute for natural materials such as ivory, bones, amber... and its application was extended to various objects such as glasses, hair combs and also photographic films and coatings.

All polymers are intrinsically susceptible to oxidation, and artifacts suffer from degradation, which makes their long-term conservation a major concern for museums, conservators and material scientists. After several decades in microclimatic museum conditions, celluloid artifacts show spots, discolouration and yellowing, and the materials become brittle and show cracks leading to total breakdown of the artifacts [3,4] (Fig. 1). In order to propose conservation treatments that are adapted and suitably efficient for the long-term preservation of celluloid, it is of prime importance to

elucidate the degradation mechanism of this material and the consequences of the degradation on the visual and mechanical properties of celluloid artifact collections.

The degradation can be considered as the result of various reactions provoked by the stresses of the natural environment (light, temperature, humidity) of the artifacts. These reactions are likely to modify the chemical structure of the macromolecules, leading to the loss of the use properties of the polymer. The elucidation of the relationship between the modification of the chemical structure upon irradiation and the degradation of properties such as the appearance and the mechanical properties, is particularly important with respect to predicting the fate of the material.

Cellulose nitrate (or nitrocellulose, NC) is obtained by preparing nitrate ester of cellulose, which is a polysaccharide constituted of pyranose rings. The maximum nitrogen content in NC is 14.14%. It corresponds to the substitution of the three hydroxyl groups of cellulose by nitrate groups, on each pyranose ring. NC is a versatile and widely used polymer, with numerous applications. With nitrogen content less than 12%, NC was used for manufacturing photographic film and is still used for a wide range of applications as films, inks, paints. The main application of NC with nitrogen content higher than 12% is the preparation of explosive formulations as propellants [5]. NC is known to be sensitive to the action of different elements such as heat [6–11] and light [12–15].

Several papers reported studies made on old artifacts based on NC. Selwitz [16] reported on the use and the stability of cellulose

* Corresponding author. CNRS, UMR 6296, ICCF, BP 80026, F-63171 Aubière, France.

E-mail address: sandrine.therias@univ-bpclermont.fr (S. Therias).



Fig. 1. Photos of celluloid museum artifacts.

nitrate in art conservation. The author underlined the lack of basic knowledge on the stability of NC under UV degradation and therefore the need for fundamental studies on the role played by the interactions of oxygen and light on NC stability. Quye et al. [17] recently reported an analytical study of selected historical artifacts to explore the origins of their different extents of degradation. The authors highlighted a connection between the durability of the artifacts and the sulfate content remaining from the original synthetic process and also the role played by the rate of loss of the plasticizer. They detected the presence of oxalate, which implies that chain scissions of cellulose nitrate occurred. Hon et al. [12] studied the adverse effects of light irradiation on cellulose nitrate films. They compared its photochemical behaviour in a vacuum and in air and showed that in both cases the molecular weight of cellulose nitrate films was reduced and denitration of cellulose nitrate films was also observed. They also reported the yellowing of the films and that the films became brittle and could totally lose their integrity. The influence of light wavelength and the physical state (solid or in solution) of cellulose nitrate on the molecular mass changes was also studied [16].

The results reported in this article aim at characterizing the consequences of the chemical modifications provoked by photodegradation on the macroscopic properties of the polymer and to qualitatively and quantitatively elucidate the relationship between the chemical modifications and the degradation of the material properties. The properties of interest are the optical and the mechanical properties, which are particularly important if one considers the applications of celluloid in the domain of artworks.

The main objective of this work was to provide a mechanism accounting for the photodegradation of celluloid. This mechanism should explain the modification of the chemical structure and account for the formation of the major oxidative species. With this objective, the photodegradation of cellulose nitrate (NC) and cellulose acetate (CA) was studied. Cellulose acetate (CA) was chosen to highlight the specific reactivity of nitrate substituent groups.

2. Experimental

2.1. Materials

Cellulose nitrate (NC) films were made from membranes purchased from GE Healthcare (US). The quantitative elemental analysis indicated weight percents of carbon, hydrogen and nitrogen of 27.20%, 2.93% and 11.76% respectively. Consequently, this sample should contain 2.2 nitro groups per glucopyranosyl unit of the cellulose. Films of NC, with thicknesses between 10 and 60 μm (measured using a CADAR-MI20 μm), were obtained from solutions in THF (NC was dissolved by heating at 45 $^{\circ}\text{C}$ for 90 min) at a

maximum concentration of 10 g L^{-1} . After solution casting, by using a coat-master (Erichsen Coatmaster 809 MC) films were left drying in ambient air for at least 24 h. Thin samples (thickness less than 10 μm) were obtained with a few droplets of dilute solutions deposited on KBr windows. Celluloid (C) was obtained from a THF solution of cellulose nitrate (NC was dissolved as previously described by heating at 45 $^{\circ}\text{C}$ for 90 min) added with camphor (Aldrich), with a ratio of 70/30 in weight. The obtained blend contained 30% by weight of camphor. Films and thin samples were prepared using the same *modus operandi* as given for NC samples. The quantity of camphor in the samples was checked by infrared spectroscopy and determined from a calibration curve between the ratio of absorbance at 1730 cm^{-1} /1655 cm^{-1} and the camphor concentration in a cellulose nitrate film using the following equation:

$$(A_{1730}/A_{1655}) = 0.013 \times (\% \text{ of camphor})$$

The chemical structures of cellulose nitrate (NC) and camphor used in this work are reported in Fig. 2.

Cellulose triacetate (Fluka) ($T_g = 220$ $^{\circ}\text{C}$) was used as received to prepare films from CHCl_3 solution by drop casting.

2.2. Accelerated weathering

2.2.1. UV light irradiation

NC and CA thin films (4–30 μm thick) were submitted to artificial accelerated photodegradation under UV–visible light irradiation ($\lambda > 300$ nm, 60 $^{\circ}\text{C}$) in ambient air. Irradiations ($\lambda > 300$ nm) of the thin films were performed in a SEPAP 12/24 unit, which was designed for studying polymer photodegradation in artificial ageing with medium-accelerated conditions. These accelerated degradation conditions are representative for outdoor weathering and as they are even more drastic degradation conditions than those in museums ($\lambda > 340$ nm), they were chosen to study both

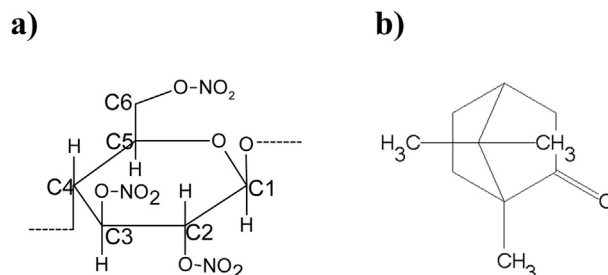


Fig. 2. Chemical structure of (a) cellulose nitrate (NC) and (b) camphor.

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