



Photooxidation of cellulose nitrate: New insights into degradation mechanisms



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H I G H L I G H T S

- The photooxidation of cellulose nitrate was focused on the formation of polluting chemical products.
- Chemical modifications revealed de-nitration of cellulose nitrate and formation lactone and anhydride.
- Correlation between modifications in chemical structure and thermal functional properties.

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Cellulose nitrate (or nitrocellulose) has received considerable interest due to its uses in various applications, such as paints, photographic films and propellants. However, it is considered as one of the primary pollutants in the energetic material industries because it can be degraded to form polluting chemical species. In this work, the UV light degradation of cellulose nitrate films was studied under conditions of artificially accelerated photooxidation. To eliminate the reactivity of nitro groups, the degradation of ethylcellulose was also investigated. Infrared spectroscopy analyses of the chemical modifications caused by the photooxidation of cellulose nitrate films and the resulting formation of volatile products revealed the occurrence of de-nitration and the formation of oxidation photoproducts exhibiting lactone and anhydride functions. The impact of these chemical modifications on the mechanical and thermal properties of cellulose nitrate films includes embrittlement and lower temperatures of ignition when used as a propellant.

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1. Introduction

Cellulose nitrate, or nitrocellulose (NC), is known as a versatile, widely used polymer with numerous applications. NC is obtained by preparing a nitrate ester of cellulose, a polysaccharide composed of pyranose rings. The maximum nitrogen content in NC is 14.14%, which corresponds to the replacement of the three free hydroxyl groups of cellulose with nitrate groups on each pyranose ring. With nitrogen content of less than 12%, NC is used for manufacturing photographic films, inks, and paints. The primary application of NC with nitrogen contents higher than 12% is in the preparation of explosive

formulations as propellants [1]. NC is considered as one of the main pollutant in energetic materials industries and the presence of nitro compounds materials in the waster effluent causes severe environmental problems, high toxicity. NC has been found to be sensitive to various elements, including heat [2–7] and light [8–10]. Therefore controlling NC degradation is essential to ensuring environmentally friendly waste management [11] as well as the stability of the NC properties [12].

Although the thermal decomposition of NC has been widely investigated in terms of its mechanism and kinetics, the light sensitivity of NC has received considerably less attention. During primary decomposition, NO₂ is released and three fully nitrated pyranose rings disintegrate, inducing chain scission reactions [2,4–7,10]. During secondary degradation, NO₂ acts as an oxidiser [6,7,10]. The reactions rates of secondary degradation are faster than those of primary decomposition, particularly when UV-light and oxygen are provided because light reduces NO₂ to NO and

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singlet oxygen, two highly reactive species [10]. The formation of carbonyl functions [4,5,8] on cellulosic backbones and the occurrence of cross-linking reactions [8] have been reported but were not extensively investigated. Thus, a mechanism for the chemical modifications of NC during thermal- and photodegradation that accounts for the primary oxidation species has yet to be proposed.

The main objective of this work was to provide a detailed degradation mechanism for cellulose nitrate (NC) under photoaging that explains the modification of its chemical structure and accounts for the formation of known oxidative species. Within this objective, diethyl cellulose (EC) was studied as a model polymer of NC. EC was chosen to highlight the specific reactivity of the nitrate substituent groups. NC and EC thin films (4–30 μm thick) were submitted to artificially accelerated weathering under UV-vis light irradiation ($\lambda > 295 \text{ nm}$, 60°C) in ambient air. The resulting chemical modifications were investigated by IR spectroscopy. The photoproducts were identified by various analytical measurements of the oxidised films combining physical and chemical derivatisation treatments coupled with IR spectroscopy. Identification of the low molecular weight products was performed by head-space solid-phase micro-extraction (HS-SPME) coupled with GC-MS analysis and ion chromatography experiments. Another goal of this work was to elucidate the qualitative and quantitative relationship between the modification of the chemical structure upon irradiation and the degradation of the materials properties of NC, such as its thermal properties, which are particularly important in predicting the fate of the material.

2. Experimental

2.1. Materials

2.1.1. Cellulose nitrate and ethyl cellulose films

Nitrocellulose and ethylcellulose (EC) are produced from cellulose. These polymers are composed of D-glucopyranose units linked by glucosidic bonds with a $\beta(1-4)$ conformation. The structural differences from cellulose consist of the groups present on carbons C2, C3 and C6 [13]. These three positions, in the case of nitrocellulose, can be occupied by nitro groups rather than hydroxyl groups, or by ethoxy groups in the case of EC. The chemical structures of these polymers depend on the relative ease of substitution at each site and on the average number of substituted groups in each pyranose unit. Substitution reactions on cellulose are statistical, allowing the monomers to undergo varying degrees of substitution.

Cellulose nitrate (NC) films were made from membranes purchased from GE Healthcare (US). Quantitative elemental analysis indicated weight percentages 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. Ethyl cellulose (EC) containing 2.5 ethoxy groups per glucopyranosyl unit was supplied by Scientific Polymer Products. According to the literature [13,14], for a substitution degree higher than 2, the most

representative monomer is tri-substituted. Accordingly, the chemical structures of NC and EC used in this work are depicted in Fig. 1.

Films of NC and EC with thicknesses of 10 and 60 μm , respectively, were obtained from solutions of THF and chloroform at a maximum concentration of 10 g l^{-1} . Following solution casting using a coat-master (Erichsen Coatmaster 809 MC) for the NC samples and Petri boxes for the EC samples, the films were allowed to dry in ambient air for a minimum of 24 h.

Thin samples (thickness less than $10 \mu\text{m}$) were obtained by depositing a few droplets of dilute solution on KBr windows.

2.1.2. "Impregnated" diethylcellulose films

To identify the degradation products, EC films blended with low molecular weight species that were potential oxidation products of the polymer, such as gluconolactone (Sigma-Aldrich) and glucuronic acid (Sigma-Aldrich), were prepared in methanol and chloroform, respectively. Blends of EC and poly (maleic anhydride alt 1 octadecene) were prepared in chloroform, and free-standing films were obtained after at least 24 h of drying in ambient air.

2.2. Accelerated weathering

2.2.1. UV light irradiation

The UV-vis light irradiation ($\lambda > 295 \text{ nm}$) of the films was performed in an irradiation device, the SEPAP 12/24 unit (ATLAS) that was designed for studying polymer photodegradation under artificial ageing with medium-accelerated conditions [15]. The chamber consisted of a square reactor equipped with four medium-pressure mercury lamps (Novalamp RVC 400 W) situated vertically at each corner of the chamber. Wavelengths below 295 nm were filtered by the glass envelope of the lamps. In the centre of the chamber, the samples were fixed on a 13-cm diameter rotating carousel that could hold up to 24 samples. In this set of experiments, the temperature at the surface of the samples was fixed at 60°C . Irradiation in the absence of oxygen (photolysis experiments) was performed on samples introduced into borosilicate tubes and sealed under a vacuum of 10^{-4} Pa with a diffusion vacuum line. The samples under vacuum in the tubes were then placed in the SEPAP 12/24 device for ageing.

2.3. Characterisation

2.3.1. Infrared analysis

IR spectra were recorded in transmission mode with a Nicolet 6700 Fourier transform infrared (FTIR) spectrophotometer operated with the OMNIC software. The spectra were obtained with 32 scan summations at 4 cm^{-1} resolution. The IR absorption band corresponding to the acetal structure at 1070 cm^{-1} was used as a reference for the film thickness.

IR-ATR (Attenuated Total Reflectance) spectra were recorded in reflection mode with a Nicolet 380-FTIR spectrophotometer equipped with a Thunderdome-ATR (4 cm^{-1} , 32 scans). The Thunderdome is a single reflection ATR accessory with a diamond crystal (depth analysis $\sim 2-3 \mu\text{m}$).

2D FTIR correlation spectroscopy was performed using the commercial software SpectraCorr from Thermo Scientific. The theory and methodology of 2D FTIR spectroscopy are summarised elsewhere [16]. Briefly, IR spectra were recorded at different ageing times, and the spectrum of the un-aged sample was used as a reference and therefore subtracted from each spectrum prior to the calculations. The complex cross correlation intensity was calculated by the software. The real part (synchronous correlation) and imaginary part (asynchronous correlation) are reported in this work.

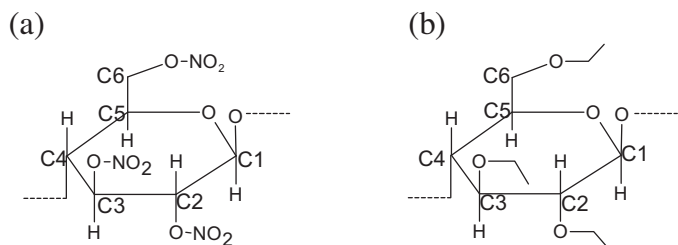


Fig. 1. Chemical structures of the polymers (a) NC and (b) EC.

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