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The effect of light on the viscosity and molecular mass of nitrocellulose

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ABSTRACT

The photodegradation of a series of nitrocellulose (NC) samples with nitrogen contents ranging from 11.69% to 13.55% has been investigated by observing changes in molecular mass and viscosity using, respectively, size exclusion chromatography (SEC) and a modified cone and plate rheometer. When NC in γ-butyrolactone was subjected to UV light in the range 320–390 nm its specific viscosity (η_{sp}) was found to decrease noticeably, a change attributed to polymer chain scission and de-aggregation. This view was supported by an observed reduction in the mass average molecular mass (M_w). In contrast, irradiation with a single wavelength at 365 nm did not significantly change either η_{sp} or M_w and similar behaviour was observed when NC solutions were irradiated with visible light (400–500 nm). In the solid state, the photodegradation of water-wet NC is faster than that of the dried material, which is attributed to the catalytic effect of acids formed from the reaction between water and nitrogen oxides (NO_x) arising from NC decomposition. A higher degree of crystallinity in the NC, as found by X-ray diffraction (XRD), was shown to lead to a smaller decrease in viscosity and molecular mass. This is thought to be because the photodegradation reaction is suppressed in crystalline NC by more effective radical–radical recombination.

1. Introduction

Nitrocellulose (NC) is an important industrial polymer manufactured by nitrating the hydroxyl groups of naturally occurring cellulose. It has many applications, the nature of which depends on its degree of nitration or nitrogen content. At low nitrogen contents (below ~12.2%) it is used in cosmetics, printing inks, paints and lacquers while at nitrogen contents above ~12.2% it is used as an energetic ingredient in gun and rocket propellants [1]. At ambient temperature NC undergoes slow decomposition to give NO_x, which generates acids that act as catalysts for further decomposition, ultimately leading to auto-ignition [2]. The prevention of autocatalytic decomposition during storage of propellants is achieved by incorporating stabilizers such as aromatic amines [3] or urea derivatives [4] that react rapidly with the NO_x. A great deal of research has been carried out on the thermal decomposition of NC and the process has been well characterised [5–11]. In comparison the photo-decomposition of NC has received much less attention.

Abel first established that nitrocellulose is sensitive to light in 1867 [12]. He found that guncotton was converted to a brown gum-like material with a high acid content. It was later shown that the influence of some forms of electromagnetic radiation on NC leads to rapid nitrate ester group loss together with polymer chain scission and cross-linking [13]. Hon and Gui reassessed the photodegradation of NC in 1986 by determining the molecular mass of the material in vacuum and in air [14]. However, they did not control the irradiation time or the intensity of light and no assessment was made of changes in the mechanical properties of the NC over time. There were also apparent irregularities in the reduction of molecular mass during the first few hours of exposure to air. In a more recent study Ng and Yu reported that NC did not change significantly when films containing the polymer were irradiated with X-rays [15]. In a report on the physical–mechanical properties of nitro-dopes subjected to UV radiation Cakić *et al* [16] measured the molecular mass and viscosity changes in the NC-based material but the influence of the power and intensity of the UV light used and of other components in the composition were not considered.

The source of cellulose and its history influences the molecular mass and mechanical properties of the NC derived from it. Cellulose degradation during growth and production over different seasons and geographical locations is affected by the prevailing weather conditions, including the amount of sunlight received [17]. Once it is produced NC is normally stored in water-wet form and under these conditions, even in diffused light, it undergoes some photodegradation. However, the nature and the extent of degradation are not fully understood. The study of NC photodegradation may therefore help to identify suitable sources of cellulose for

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propellant grade NC manufacturing and lead to recommendations for more appropriate storage conditions.

In this paper we report the results of viscosity measurements on NC solutions subjected to irradiation by UV and visible light. The molecular mass changes of the NC following irradiation, measured by size exclusion chromatography (SEC), have also been reported. A custom-modified cone and plate rheometer enabled *in-situ* continuous viscosity measurements to be made under a temperature-controlled environment and gave results with a precision of ±0.5%. The effects of different wavelengths of UV and visible light on the extent of NC decomposition and on the associated viscosity and molecular mass changes have also been described. The rates of photodegradation in dried and water-wet solid NC samples were investigated and compared. The influence of crystallinity on NC degradation has also been explored.

2. Experimental

2.1. Materials

Nitrocellulose samples with quoted nitrogen contents of 11.69%, 12.15%, 12.71% and 13.55% were obtained from Nitrochemie (Wimmis, Switzerland) and carefully dried by placing about 10 g of each under vacuum for 2.5 h at 65 °C followed by a further period of 17 h under vacuum at room temperature. Tetrahydrofuran (99.99% stabilised with 100 ppm butylated hydroxytoluene [2,6-bis(1,1-dimethylethyl)-4-methylphenol, BHT], Rathburn Chemicals Ltd, Walkerburn, Scotland, UK) and γ-butyrolactone (99.9%, Sigma–Aldrich, Gillingham, Dorset, UK) were employed as solvents for NC and were used as received. The dried NC was dissolved in γ-butyrolactone at different concentrations by mixing the two materials at room temperature in the dark over 7 days with occasional gentle shaking. γ-Butyrolactone was chosen for the viscosity measurements since it is a good solvent for NC and has a low vapour pressure.

2.2. X-ray diffraction analysis

X-ray diffraction analysis was carried out on four NC samples with nitrogen contents between 11.69% and 13.55% using a PANalytical X'Pert PRO Multi-Purpose Diffractometer with Cu Kα radiation. A PIXcel detector was used to collect data over an angular range of 10–80°/2θ with a step size of 0.0131°/2θ and a count time of 49.470 s at each step. The voltage was chosen to be 40 kV with a current of 40 mA. Powdered specimens were prepared for X-ray diffraction analysis using the PANalytical PW1770/10 Powder Sample Preparation Kit and back-loaded into nickel-coated steel sample holders (PW1811/16 with PW1811/00 bottom plate).

2.3. Size exclusion chromatography

Polystyrene (PS) equivalent molecular masses were determined using a size exclusion chromatography (SEC) system employing a VE 1121 solvent pump (Viscotek Corporation, Houston, Texas, USA), a DEG-104 solvent degasser (Kontron, Eching, Germany), a 2410 refractive index detector, column heater and 717+ auto sampler injector (Waters, Milford, Massachusetts, USA). The column length was 300 mm with a diameter of 7.5 mm and was packed with PL-gel 10 μm mixed-B phase (Polymer Laboratories, Church Stretton, Shropshire, UK). Tetrahydrofuran was used as the eluent at a flow rate of 1 ml min^{-1} and a temperature of 35 °C. The SEC data were processed using Waters Millennium Empower software. A calibration curve was constructed using polystyrene standards (EasiCal PS1™, Polymer Laboratories) that covered a molecular mass range from 580 to 7.5×10^6 g mol^{-1}. The relative standard deviation of the molecular masses of the nitrocellulose samples was less than 5%.

2.4. Irradiation of nitrocellulose

The NC samples in the solid state and in solution were irradiated using a Novacure M2100 light source (EXFO Photonic Solutions Inc, Mississauga, Ontario, Canada) with a 5 mm diameter light guide. The output from the light source was filtered to a wavelength range of 320–390 nm and a single wavelength of 365 nm for UV and to a wavelength range of 400–500 nm for visible light. The distance between the samples and the light guide was 5 cm. The NC solutions were irradiated in the rheometer for 30 min at a light intensity of 500 mW cm^{-2}. Solid NC samples were prepared by placing a small amount of the powdered material in a glass vial (20 ml capacity, 18 mm diameter) and tamping it down with a glass rod to a depth of about 1 mm. The samples were then irradiated inside the vial for 30, 52, and 92 min at a light intensity of 1000 mW cm^{-2}.

2.5. Viscosity measurements

Viscosity measurements on NC solutions were made using a Bohlin CVOR 150-HR rheometer (Malvern Instruments Ltd, Malvern, UK) with a custom-modified UV cell [18] under the controlled stress mode. A small volume of solution (340 μl) was used for each measurement. The UV cell consisted of a quartz lower plate surrounded by a water jacket and an aperture to permit irradiation via a light guide. All the viscosity measurements were performed using 40 mm diameter 1° cone geometry. A KTB30 water bath (Julabo, Seelbach, Germany) was used to control the temperature of the solution in the cell during irradiation. A schematic of the modified cell is shown in Fig. 1.

Solution viscosity was measured in the dark for 15 min to allow an initial steady-state value to be recorded. Measurements were

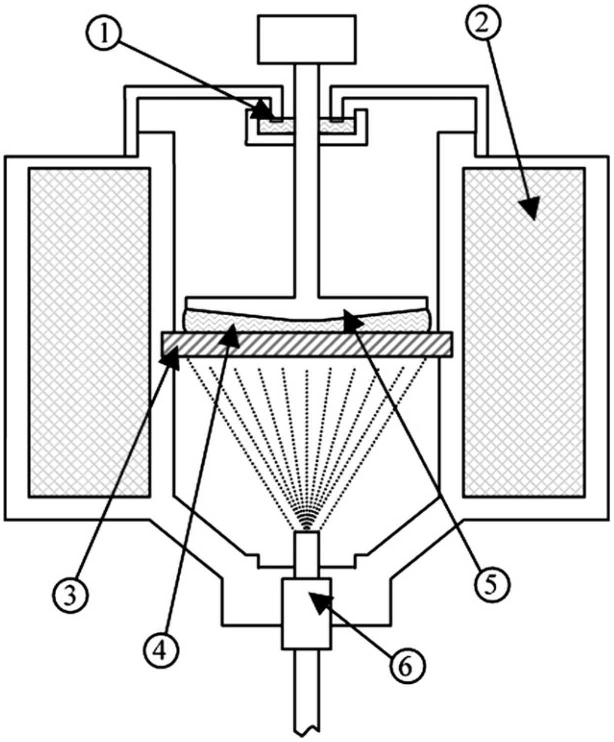

Fig. 1. Schematic of modified rheometer cell: 1, solvent trap; 2, water jacket; 3, quartz plate; 4, sample; 5, 40 mm diameter 1° cone; 6, light guide.