

Appendix 2: Detailed Experimental Procedures for Cellulose Nitrate Film Accelerated Aging Experiments

Materials. All chemicals were purchased from Sigma Aldrich (Milwaukee, WI) and used without further purification unless otherwise noted. Elemental analyses of film samples assaying for carbon, hydrogen, nitrogen, and sulfur were conducted by Columbia Analytical (Phoenix, AZ). BAM Fallhammer tests and BAM Friction Tests were conducted by Chilworth Technology, Inc. according to the specifications prescribed by the 2009 *United Nations Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria* (5th edition, 2009; <https://www.unece.org/fileadmin/DAM/trans/danger/publi/manual/Rev5/English/ST-SG-AC10-11-Rev5-EN.pdf>, accessed on Dec. 1, 2015)

Film Sample Preparation. Film frames were subjected to physical and chemical property testing in their native form with any gelatin (or emulsion layer) intact, or they were treated with bleach to remove the emulsion layer to enable testing of the cellulose nitrate base alone. The emulsion layer was removed by treatment with Tough Guy™ ultra bleach for 30 min, followed by exhaustive washing with deionized water and drying under vacuum at 22 °C. We have carefully noted in the text of this report when we have handled native film samples or ones wherein the emulsion layer was removed.

IPI Acidity Test. pH testing on the film was performed according to the method established by the Image Permanence Institute (IPI). Briefly, a 4 mm x 18.5 mm piece (50 mg) of unbleached film was cut and submerged in 5 mL of MilliQ water (> 18 MΩ resistance) in a tightly capped 20 mL scintillation vial. After 24 h at 22 °C, the pH was measured using an EMD colorpHast® pH-indicator strip (pH range 2.0–9.0).

Size-Exclusion Chromatography (SEC). SEC analyses were performed on a home-built system equipped with two Polymer Labs PolyPore 300 x 7.5 mm columns and a Waters 410 Differential Refractometer, operating with DMF with 0.1 M LiBr dissolved as the eluent at a flow rate of 0.8 mL/min. In all analyses, the columns and detector were thermostatted at 70 °C and 50 °C, respectively. A molecular weight calibration curve was constructed either ten narrow molecular weight poly(styrene) standards or seven narrow molecular weight poly(methyl methacrylate) standards ($M_n = 580\text{--}377,400$ kg/mol), in order to determine the molecular weight distributions ($\mathcal{D} = M_w/M_n$) for all of the bleached cellulose nitrate samples (emulsion layer removed). Data was acquired using a NI USB-6008 DAQ (analog to digital converter) and a custom LabView (National Instruments Co.) interface written by Adam Schmitt. The data was calibrated and analyzed using a custom procedure written in Igor Pro (https://figshare.com/articles/Computer_Code_for_Materials_Scientists_Igor_Pro_Procedures_for_Analyzing_Dynamic_Light_Scattering_Rheology_and_Synchrotron_X_ray_Scattering_Data/644515).

¹H NMR. ¹H NMR spectra were acquired in DMSO-*d*₆ or acetone-*d*₆ on an Avance-400 spectrometer operating at 400 MHz with a pulse repetition delay of at least 10 s. Spectra were referenced to the residual protiated solvent peak in each sample. These

spectra were quantitatively integrated in order to determine chemical changes to the structure of the cellulose nitrate film.

Thermogravimetric analysis (TGA). The thermal stability of each cellulose nitrate film was measured in a TA Instruments Q500 Thermogravimetric Analyzer using a ramp rate of 10 °C/min under an O₂ (g) purge (20 mL/min) over a temperature range of 25-250 °C followed by a temperature jump to 600 °C to ensure complete sample combustion. The typical mass of the film sample used for each TGA run was ~3-5 mg.

Differential Vapor Sorption (DVS). Water uptake measurements as function of relative humidity at 30.0 °C and 60.0 °C made using a TA Instruments Q5000SA dynamic vapor sorption analyzer. At each relative humidity condition between 5–95 %RH, the water uptake of the sample was monitored by measuring the mass increase upon equilibration for 20 min. These measurements were made in the laboratory of Prof. M. A. Hickner of the Department of Materials Science Engineering at Penn State University (State College, PA).

Accelerated Aging studies. For each accelerated aging trial conducted at 60 °C and a given relative humidity condition, we prepared one 32 oz., wide-mouth jar equipped with Teflon-lined polypropylene cap. Each jar was loaded with seven (7) 1" x 4" inch borosilicate test tubes. We then made six (6) film packets, each comprising five (5) consecutive film frames of similar condition that were bound together into a stack using Teflon-coated copper wire threaded through the sprocket holes. These packets were intended to mimic a roll of film in a smaller physical footprint format compatible with the oven selected for the elevated temperature, long-term aging experiment. Each of one of these six packets was loaded into a different test tube in the 32 oz. glass jar. The seventh test tube was loaded with a saturated water/salt solution, whereby the use of different salts enabled establishment of different relative humidity conditions within each sealed aging containers. According to literature references from the National Institute of Standards and Technology (NIST), we used MgCl₂, NaBr, and KCl saturated salt-water solutions (~3.0 g of salt in ~12 mL MilliQ water) to produce 30, 50, and 80 % RH environments, respectively, at 60 °C. One sample jar was prepared for each of **CN-0** aged at 30 %RH, **CN-0** at 50 %RH, **CN-0** at 80 %RH, **CN-2** at 80 %RH, **CN-4** at 80 %RH. Note that the **CN-4** jar contained only one stacked film packet, as we sought to test only the 360 day aging time point for this already degraded sample. These five separate jars were loaded into a Thermo Scientific Lindberg Oven equipped with a built-in digital microprocessor for controlling the temperature at $T = 60.0 \pm 0.1$ °C. We monitored the relative humidity at least three times weekly using a NIST-calibrated Fisherbrand hygrometer (Fisher Scientific, Inc.). The measured relative humidity in each container was within ± 5 %RH of the target value. At each time point (15, 30, 60, 90, 180, and 360 days), we carefully removed the glass jar from the oven, opened it in a fume hood to vent any noxious gases, and removed one film sample packet from the container. **CAUTION: Gases evolved in this experiment are toxic! Inhalation of nitric acid vapors can lead to permanent respiratory damage, including permanent loss of the sense of smell.** The remaining samples were left in the container, which was resealed and returned to the 60 °C oven to continue the aging experiment.

Upon removing each film packet from the controlled accelerated aging environment, the samples were stored in Ziploc bags and subjected to testing protocols described above in either their native form (emulsion layer intact) or bleached form (emulsion layer removed) as soon as possible.