Analysis of the Physical Characteristics of Transparent Cellulosic Nanofiber Paper

Introduction

Handling works of art on paper can present many challenges for conservators, due to the inherent fragile nature of paper. Conservators must not only take into consideration the limitations of the physical properties of the materials, but must also resolve specific exhibition, aesthetic, and storage concerns related to the work of art.

Often, contemporary works of art on paper push the boundaries of historical art aesthetics, when the physical properties of the substrate material become vital to the conceptual interpretation of the work. A visual dialogue between the spectator and the object is created by the tactile nature and inherent sense of fragility that paper possesses. These characteristics can be further manipulated by exaggerating the dimensions of the work of art beyond traditional formats and exhibiting the work unframed and fully exposed to the surrounding environment. Aesthetic and conceptual intent, in relation to the size, weight, transparency, and stability of a work of art on paper, must all be considered when preparing the object for exhibition. In particular, the degree of transparency of the substrate material will dramatically influence, and quite often limit, the mounting and exhibition options available to the conservator.

Hinging a work of art to a secondary support is traditionally achieved by selecting a hinging tissue and adhesive that is chemically stable, easily reversible, and an appropriate weight for the work of art. Hinges should not be of a heavier or stronger material than the art work itself, while at the same time, the hinge must be able to provide adequate support. The addition of any new material "must ensure the preservation of the physical and historical integrity of a given object and contribute to its chemical stability." An inappropriate hinging material or method could cause damage to the object by inducing planar deformations, tearing, staining, and color change. The overall aesthetics of the work can also be interrupted by the degree of visibility the hinging tissue has through more translucent materials.

The following research project investigates the physical characteristics of optically transparent cellulosic nanofiber paper as an alternative conservation-grade material for the hinging and exhibition of translucent or oversized works of art on paper.

Transparent Cellulosic Nanofiber Paper

Transparent cellulosic nanofiber paper is structurally composed of cellulose microfibrils, which are the main constituents of plant cell walls. Nanofibers are characteristically different from traditional paper fibers in two fundamental ways: 1) the fiber width; and 2) the size of the interstitial cavities, or air pockets, between the fibers. Nanofibers are dimensionally smaller due to their individual microfibril composition, when compared to the microfibril bundles that form larger fiber structures. Secondly, nanofibers in optically transparent papers, are densely packed which greatly reduces the size of the interstices between the fibers. The scanning electron micrograph (SEM) image in Figure 1 is of a Kozo Japanese paper, while the SEM image in Figure 2 is of transparent nanofiber paper at the same magnification. What becomes immediately apparent is the difference between the fiber size in both images. The Kozo fibers are easily imaged at this magnification, where as the transparent nanofiber paper produces a topographic image of the surface texture, with no indication of nanofibers.

The optical transparency of nanofiber paper is achieved through the reduction of scattered light, both internally and superficially. This phenomenon is made possible by three factors, the aforementioned small fiber width and reduction of interstitial cavities between the fibers, and the ability to obtain a highly polished surface. Nanofibers "are free from light scattering due to their diameters being less than one-tenth of the visible light wavelength." Furthermore, "if the cellulose nanofibers are densely packed, and the interstices between the fibers are small enough to avoid light scattering, the cellulosic material becomes transparent."

When one compares Figure 1 with the atomic force micrograph, or AFM, phase view image in Figure 3 of a transparent nanofiber paper, note the scale difference between the two

Figure 1

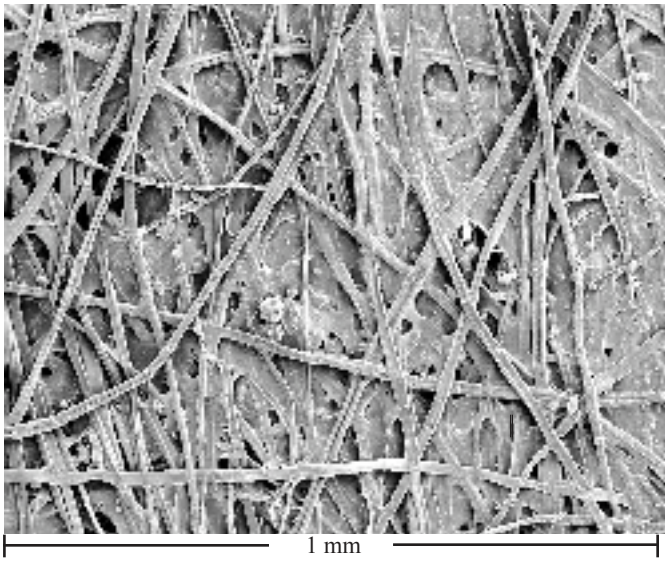
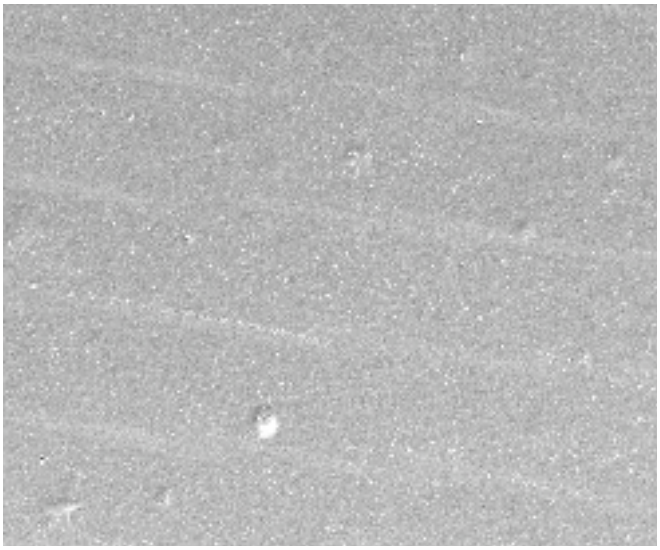


Figure 2



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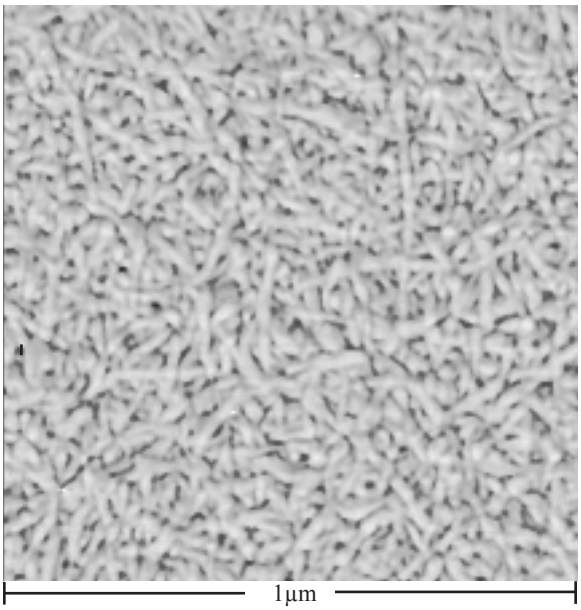
images from 1mm to 1μm. In order to image the nanofibers, AFM imaging was required because the technique has the ability to scan the surface of a sample using a silicon tip mounted to a cantilever to produce topographic images with nanometer resolution. When the two images are compared the difference between fiber size and the interstitial cavities between the fibers is evident.

Figure 3



Current Trends

Nano-technology is in the beginning stages of its development, and analytical testing of the physical, chemical, and mechanical properties of nano-materials continues to be evaluated. The manufacture of nanofibers resides within the domain of paper engineering laboratories of select international institutes, and at present the material is not commercially available.

One of several current trends for the development of nano-technology is the assessment of the material as a possible replacement for glass substrates and viewing screens in electronic devices. Traditionally, glass has been used in electronics because it has a low coefficient of thermal expansion (CTE) of 8.5 ppm K-1; glass can sustain the heat produced on the assembly line during manufacturing processes and the heat produced by the component parts when the electronic device is in use. Furthermore, glass is readily available and can be manufactured transparent for use in display screens. Interestingly, what is of more significance in this particular discussion are the limitations of the glass components, which are that glass is heavy, rigid, and fragile. These limitations are what have helped foster the research and development of transparent nanofiber paper technology.

Other areas of research for nano-technology include, but are not limited to: 1) the medical field where nano-technology is being evaluated for tissue defect repair; 2) the addition of nanofibers for the reinforcement of adhesives; 3) the addition of nanofibers as a strengthening agent in foams, aerogels, and starch; and 4) advances in material reinforcement, such as fiberglass, in the aerospace and automobile industries.

To date, nano-technology has not been much investigated in terms of possible art conservation applications. The current analytical data indicates that nanofiber materials exhibit similar physical characteristics as traditional fiber-based papers. They are hygroscopic and foldable, but they also exhibit some very unique characteristics such as a low coefficient of thermal expansion, similar to glass, and an ability to obtain various degrees of optical transparency while maintaining fiber density and tensile strength. This is in sharp opposition to the ways in which transparency in papers have previously been obtained, either by reducing the density of the packed fibers or by chemically processing the paper.

Preparation of Transparent Nanofiber Paper

The transparent nanofiber paper obtained for testing was manufacture into sheet form by Houssine Sehaqui, PhD candidate, Royal Institute of Technology (KTH), Fiber and Polymer Technology, Division of Biocomposites, Sweden. The nanofibrillated cellulose (NFC) water suspension was prepared from a softwood sulphite pulp, manufactured by Nordic Pulp and Paper, Sweden, with a composition of 0.7% lignin and 13.8% hemicelluloses.

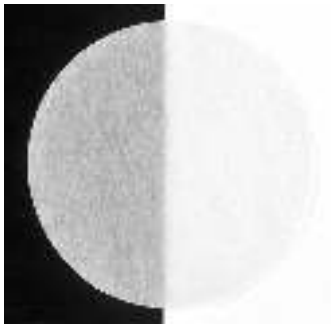
In total, eleven samples were prepared for analysis. Ten were used for testing and one was kept as a reference sample. The samples were 7cm in diameter, with a random fiber distribution. They are approximately 53μm thick and weighed 257mg. The samples were pre-conditioned in the dark for three days before analysis (Figure 4).

Preparation of Kozo Kurotani #16 Paper

A conservation-grade Kozo Japanese paper, Kurotani #16, was selected for comparative analysis and was purchased from the Japanese Paper Place, Toronto, Ontario. Kozo is a bast fiber obtained from the inner bark of the paper mulberry bush. The inner bark is what gives the plant stem its rigidity because these are the longest and strongest fibers of the stem, which measure approximately 10 - 15 mm in length. Papers made from Kozo fibers exhibit exceptional permanence and durability and are appropriate for almost any paper conservation technique because of their wet strength, their long, strong fibers, and their malleability.

Figure 4

Figure 5



In total, thirty samples were prepared for analysis from the same sheet of paper. The samples were 7cm in diameter, with a directional fiber distribution. They are approximately 61μm thick and weighed 69mg. The samples were also pre-conditioned in the dark for three days before analysis (Figure 5).

Instrumental Analysis

Instrumental analysis of the prepared samples was conducted at both the Canadian Conservation Institute in Ottawa, Ontario and at Queen's University, Kingston, Ontario. Analysis included: 1) UV aging, where light from a xenon-arc lamp was used to expose the test specimens to elevated light levels over 48 hours. The light source was chosen to simulate natural day light that had passed through a window. The temperature at the surface of the test papers was maintained at 41°C for the full duration of the exposure; 2) thermal aging, which occurred over 14 days at 90°C and 70% relative humidity; 3) optical properties, before and after aging, to assess changes in opacity, brightness, and yellowness; 4) chemical properties, before and after aging, to assess changes in pH and chemical composition; 5) zero-span tensile strength, which gave an indication of the strength of the individual paper fibers rather than the paper matrix as a whole; 6) sorption properties and moisture content; 7) caliper, or thickness, of each sample; and 8) fiber imaging included scanning electron and atomic force microscopy.

Results

The aim of this study was to determine the physical characteristics of transparent nanofiber paper and compare these results to a known conservation-grade Kozo, Kurotani #16, Japanese paper. UV and thermal accelerated aging was included in the analysis to help indicate the relative chemical stability and durability of the test materials before and after aging.

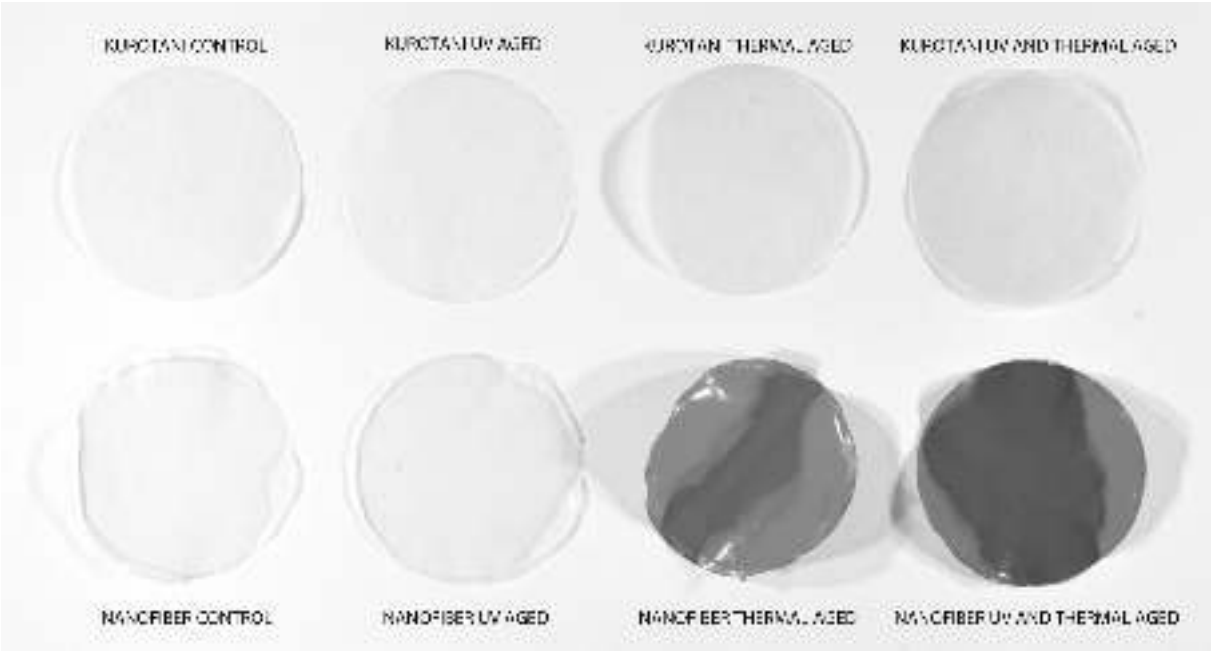
Accelerated aging, both UV and thermal, induced color change in the nanofiber and Kurotani samples. When viewed with the naked eye, the nanofiber samples appeared unchanged after UV aging, while the Kurotani samples were slightly bleached by the UV rays, and became less yellow. The most dramatic color change occurred after thermal aging when the nanofiber samples turned dark brown.

It is important to note that the thermal test conditions were quite extreme, whereby exposure at 90°C and 70% relative humidity over 14 days dramatically changed the nanofiber samples, but there was also a thermal component to the UV aging that induced little to no change in the test samples when exposed at 41°C over 48 hours.

The handling properties of the nanofiber paper was also changed following UV and thermal aging. The nanofiber samples became less ductile and increasingly brittle, which frequently caused hair line fracturing and splitting of the paper when cut with shears or folded during sample preparation for instrumental testing.

The pH testing was undertaken in this study as acidity contributes to the physical degradation of paper fibers. The pH of the un-aged nanofiber sample was 6.64, which was slightly more acidic than the Kurotani control sample, which had a near neutral pH of 6.99. Following UV and thermal aging, the pH of the nanofiber samples became increasingly more acidic. The UV plus thermal aged samples dropped in pH by almost 3/4 of a pH unit, which represents a fairly significant decrease. In comparison, the Kurotani samples maintained a near neutral pH before and after aging, indicating better overall chemical stability.

Figure 6 Exposure at 90°C and 70% relative humidity over 14 days



Following the preparation of the test specimens for pH measurements, it was noted that the nanofiber samples did swell considerably while in solution, and that the dark brown discolouration, induced by thermal aging, was partly soluble in distilled water.

The sorption properties and moisture content, at 50% relative humidity, for the nanofiber samples were significantly higher than the test results for the Kurotani samples. UV aging had little effect on the sorption properties of either material, and although thermal aging induced an overall decrease in these properties, the test results for the nanofiber paper remained significantly greater than the Kurotani samples.

The most unexpected result was obtained when the sorption properties and moisture content of the nanofiber paper was determined at the point of maximum adsorption. At 96% relative humidity, the control and UV aged nanofiber samples absorbed approximately 47.0g of water per 100g sample, where the water content in the paper amounts to almost half the weight of the entire sample. In comparison, the Kurotani samples exhibited little change in sorption properties following UV or thermal aging, with all results for moisture content measuring between 18.0g and 19.5g of water per 100g sample.

The isotherm graphs indicated that the nanofibers are very hygroscopic, and can absorb almost half their total weight in water, without turning into a gel. The ability of the nanofiber paper to absorb water to this degree is similar to the sorption properties of some adhesives, such as sturgeon glue.

The results of the zero-span tensile test gave an indication of the overall strength of the individual fibers for both the nanofiber and Kurotani samples before and after UV and thermal aging. As anticipated, the zero-span tensile strength of the nanofibers were three times greater than the Kurotani fibers, and comparable to a good quality bond paper. UV aging of the nanofiber samples seemed to have very little impact on the overall fiber tensile strength. However, after thermal aging, the fiber tensile strength dropped by one third. Although the decrease in tensile strength is significant, the measure of fiber strength still remains approximately two times greater than the Kurotani control sample.

Conclusions

Overall, the instrumental results indicated that the nanofiber paper maintained optical, mechanical, and chemical stability after UV aging. While in contrast, thermal aging of the samples induced more severe changes, causing the nanofiber paper to loose transparency, darken, and become brittle.

The dark brown discolouration of the samples, dramatically impacted the colourimetric results; including transparency, brightness, and yellowness. What components of the sample changed after thermal aging is unknown at this point and requires further research to determine. Fourier transform infrared (FT-IR) spectroscopy and atomic force microscopy did not indicated any significant changes in the compositional or morphological structure of the samples that could have contributed to the thermally induced color change. In general, the optical stability of the test samples were affected by the introduction of extreme thermal conditions over an extended period of time, and the brown discolouration is partly soluble in water. When dealing with fibers in the nanometer range any subtle shift in fiber size, density, or chemical degradation could dramatically change the optical characteristics of the material.

The second factor which was significantly affected by thermal aging was the pH results for the nanofiber samples. Perhaps buffering the nanofiber paper and introducing an alkaline reserve may help stabilize the pH.

Continued investigation into source materials for nanofiber extraction is necessary. For example, nanofibers extracted from wood sources must undergo acidic chemical processing to remove the lignin and other non-cellulosic components, and yield only 40 - 50% cellulose after processing. Whereas, cotton seed fibers, in the raw state, are 95% cellulose, and contain no lignin. When the fibers are boiled in alkaline water the wax and pectin are removed, which then yields a 99% pure cellulose fiber. Furthermore, the alkaline treatment could also be used to impart an alkaline reserve which may contribute to producing more neutral or alkaline pH results. Finally, the extraction of nanofibers from cotton seed hairs may promote improved handling and aging properties.

It is evident that nanofiber technology is in its developmental infancy, with a vast potential yet to be explored. The efforts of cross discipline collaborations will continue to foster the development of nano-materials, by cultivating and refining, some of nature's most powerful component parts. When considering the cross discipline needs of conservators, continued investigation into the suitability of nano-materials is warranted as the technology continues to be refined for use within a broad range of industries.

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