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Nanocellulose Films: Properties, Development, and New Applications for Translucent and Transparent Artworks and Documents

ABSTRACT

This paper focuses on the use of a new and promising material in art conservation—nanocellulose film. Today, nanocellulose films are used in many fields, including medicine, electronics, and the food processing industry, as a strengthening agent with high transparency and as a biological alternative to plastic films and petroleum-derived products. After characterizing the nanoparticles obtained from cellulose, this work describes the manufacturing processes, structure, and unique properties of these new materials. The study of nanocellulose films in conservation, which began in 2014 at the scientific lab of the National Library of France (BnF, Paris, France) and is now carried out at the Research Center for Conservation (CRCC, Paris, France), focuses on microfibrillated cellulose, which is one kind of nanocellulose. The study found nanocellulose films best suited for some conservation treatments when compared to traditional repair methods. Then, nanocellulose films were applied to a range of artworks and documents made of translucent and transparent supports from several French and American museum collections.

INTRODUCTION: A JOURNEY INTO THE INFINITESIMALLY SMALL

Graphic artworks and documents made of translucent or transparent supports are omnipresent in archives, libraries, and museum collections. Thin papers, tracing papers, and cellulose acetate sheets or films are a few examples (Laroque 2003). These supports are generally delicate and fragile, and the artworks and documents can very often have some structural alterations, such as tears and weaknesses or delamination of the media, which can be a major problem for handling, consultation, digitization, or exhibition (fig. 1). In many cases, traditional repair methods are not completely adapted to solve these specific problems. The field of nanotechnologies offers new possibilities with new and innovative materials. The main objective of this study is to introduce a new material in art conservation—nanocellulose films.

NANOCELLULOSE FILMS: CHARACTERIZATION, STRUCTURE, AND UNIQUE PROPERTIES

CHARACTERIZATION

Among nanoparticles that can be obtained from cellulose fibers, two main types can be clearly distinguished: cellulose nanocrystals (CNC) and microfibrillated cellulose (MFC). The main difference between these two materials is that MFC consists of both monocrystalline and amorphous regions of cellulose, whereas CNC is only composed of the crystalline part of cellulose, obtained by intense acid hydrolysis. The nomenclature for these materials is not yet clearly defined, and authors use various terminologies to designate the same product. In scientific literature, other terms for MFC include *cellulose microfibrils*, *cellulose nanofibrils*, *cellulose nanofibers*, and *nanocellulose*. Similarly, CNC may be termed as *whiskers, cellulose nanowhiskers*, and *nanocrystalline cellulose* (Guezennec 2012). Once they are in the form of films, these two materials could be considered as new kinds of paper, termed *nanopapers*.

STRUCTURE

MFC results from the disintegration of cellulose fibers. It is a material composed of an aggregate of cellulose microfibrils from some species of woods or plants, predelignified, obtained from layer S2 of the cell wall by intense mechanical treatments. Cellulose microfibrils are an assembly of linear glucan chains of cellulose, and the whole structure is stabilized by hydrogen bonds (Dufresne 2012; Guezennec 2012). Structurally, 100 molecules of cellulose compose 1 fundamental fibril, and 15 fundamental fibrils compose 1 microfibril. To have a better idea of the scale of these nanoparticles, the length of a microfibril is estimated to be between 1 and 3 μm, whereas the length of a fiber is generally around 1 mm (fig. 2). Additionally, the diameter of a fiber is generally estimated to be between 20 and 40 μm, whereas the diameter

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Fig. 1. From left to right: Emile Reynaud, *Autour d'une cabine*, 1895: Hand-painted gelatin windows with cracks and losses (La Cinémathèque Française—Dreyfuss-Deseigne); Walt Disney Studios, *Snow White*, 1937: Animation cel (detail) with delamination of the media and weaknesses (Disney Enterprises Inc.); Louis Kahn, *FDR Memorial in NYC*, 1973: Detail of a large tear visible on the thin tracing paper (CCAHA).

of a microfibril is, similar to the length, around 1000 times smaller and estimated to be between 5 and 30 nm.

PROPERTIES

To obtain nanoparticles from cellulose, the pulp is predelignified and the hemicelluloses are removed by mechanical and enzymatic treatments to get pure cellulose (at least 95% pure). Therefore, nanocellulose films are made of pure cellulose, without lignin, and have a neutral pH, always close to 7.0. The purity of cellulose in mending materials is a stability criterion that is very important in the conservation of artworks and documents on paper. In addition, MFC films can effectively transmit light and can be as transparent as a polyester film like Mylar. Even if they are slightly visible under reflected light, they are almost invisible once they are observed with transmitted light (fig. 3). This very specific optical property is due to the origin of the microfibrils used. It is also due to the small size of the pores (more than 100 times smaller than those of a traditional sheet of paper), the size of the microfibrils (with a diameter at the nanoscale), and the important density of the structure of the films (Guezennec 2012). Concerning its tensile strength, MFC has long microfibrils that are extremely thin (with a diameter from 5 to 30 nm) and are denser than regular fibers. For these reasons, MFC film has high mechanical strength. CNC films are even more transparent than MFC films, but they have slightly less mechanical strength than MFC films, as they are only composed of the crystalline parts of cellulose.

MANUFACTURING PROCESS OF NANOCELLULOSE FILMS

MANUFACTURE OF NANOCELLULOSE

The first nanocellulose suspensions were obtained following a method developed in 1977 by researchers from the Eastern Research Division of ITT Rayonier at Whippany, New Jersey.[1] They had the idea to pass a dilute cellulose wood pulp several times through a milk homogenizer (a Manton-Gaulin 15MR

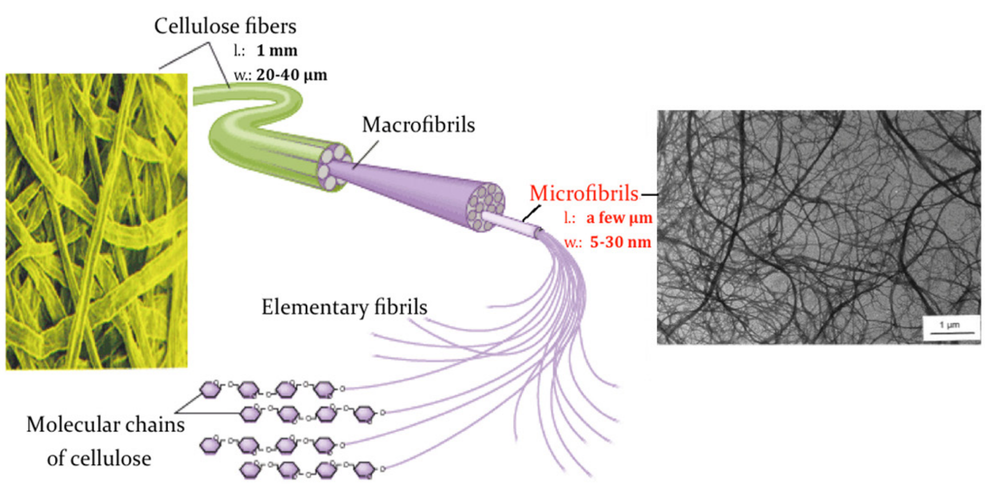

Fig. 2. Morphological structure of cellulose with the scales of fibers and microfibrils, with microfibrils observed under a TEM (Guezennec, Dreyfuss-Deseigne).

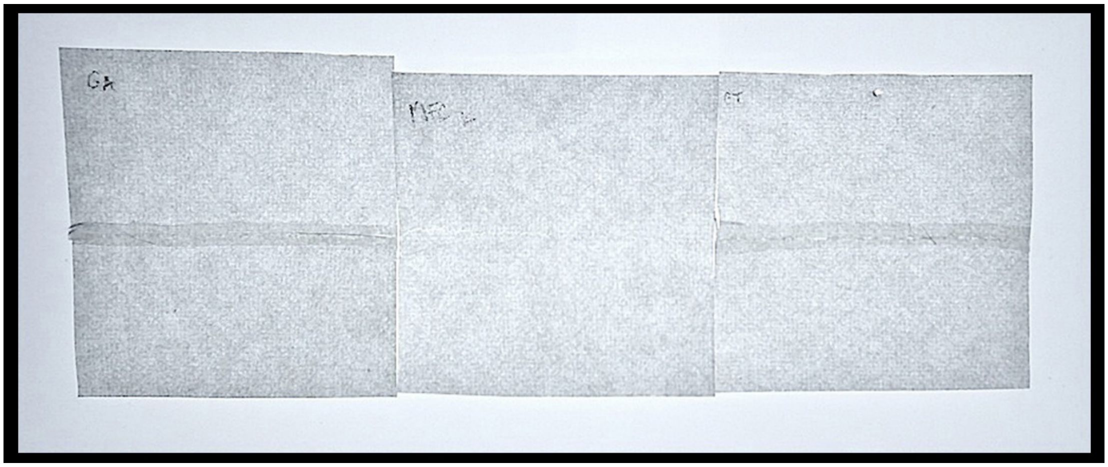

Fig. 3. Tear on a thin paper observed in transmitted light. The tear is mended with a piece of gampi 9 g/m² (left), a piece of kozo 8 g/m² (right), and a piece of MFC film (center), with the same adhesive (Klucel G in ethanol).

homogenizer), transforming fibers into a translucent gel. In fact, that mechanical treatment had broken the structure of fibers to release and obtain microfibrils. The researchers termed this new structure *microfibrillated cellulose* (MFC). Over the years, several procedures have been developed around the world for fiber delamination, where wood is always the main source used to produce MFC.

MANUFACTURE OF CELLULOSE MICROFIBRIL GEL

During this study, the author had the opportunity to visit two world major nanocellulose manufacturing facilities—the Process Development Center at the University of Maine in Orono, and the Technical Center of Paper in Grenoble, France—and to study the process closely. The method developed in 1977 consists of passing a predelignified dilute cellulose wood fiber (or paper pulp), mixed with water, several times through a mechanical homogenizer under high pressure (55 MPa) and high temperature (95°C). This important step of the process requires repeating this mechanical shearing 10 to 20 times through the double-disk refiner to extract microfibrils from fibers, increase the fibrillation, and obtain the water-based gel containing microfibrils (fig. 4). Some pretreatments of the pulp (mechanical, enzymatic, or chemical actions) are generally done to facilitate the disintegration of cellulose.

MANUFACTURE OF NANOCELLULOSE FILMS

MFC films are made from a water-based gel containing cellulose microfibrils. There are three methods for making MFC films (Guezennec 2012): (1) handsheet using a lab form, (2) filtration, and (3) casting-evaporation. The Technical Center of Paper graciously gave the author three types of 2% cellulose microfibrils from different species of trees or plants: birch kraft, spruce, and cotton. After making many MFC films, an optimal film was selected. Made of birch kraft microfibrils, the optimal film showed the necessary characteristics for conservation treatment: transparency, absence of coloration,

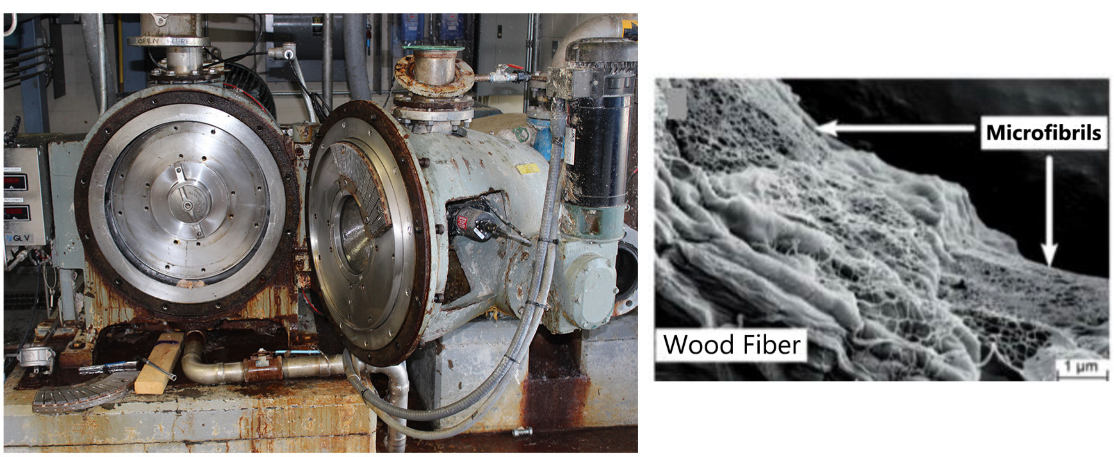

Fig. 4. Double-disk refiner at the Process Development Center at the University of Maine and microfibrils obtained from fibers.

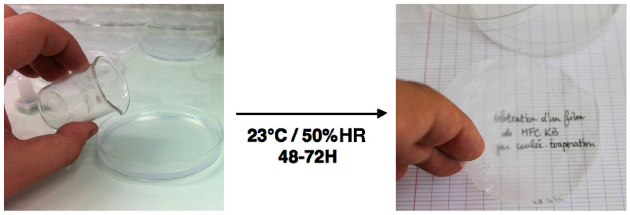

Fig. 5. Making a thin and homogeneous MFC film with the casting-evaporation technique.

homogeneity, and flexibility. After doing some tests, the casting-evaporation method of manufacture was selected due to the regularity and homogeneity of the produced films. The process was easy to reproduce, with a high yield, in a conservation lab. To make a thin film (with a thickness between 8 and 20 μm) using the casting-evaporation method, 10 g of the gel was mixed with 100 mL of deionized water to obtain a homogeneous suspension. Next, 20 mL of the suspension was poured into 90-mm polystyrene petri dishes. After 2 to 3 days of drying in a controlled environment (23°C; 50%RH), the water had evaporated and a homogeneous MFC film had formed[2] (fig. 5). These nanopapers are not dangerous to health, as they are already formed sheets, not in the form of powder or spray, and therefore its nanoparticles cannot be inhaled.

APPLICATION OF NANOCELLULOSE FILMS IN CONSERVATION

Results of tests show that MFC film has very good stability to light, temperature, and humidity aging (Dreyfuss-Deseigne 2017b). Its unique properties of transparency don't change with light, temperature and humidity aging. Additionally, a MFC film can be very thin but stronger than the thin Japanese papers generally used in paper conservation to mend translucent artworks and documents (gampi or kozo). MFC and CNC films are more sensitive to direct application of water than paper and will shrink, but they stay flat with high temperature and humidity variations. Once applied to a piece of paper with an ethanol-based adhesive, the film can be easily removed without leaving any residue behind. Considering these results, it is clear that nanocellulose films can be very suitable for mending paper objects made of translucent or transparent supports. These new materials were used for the first time during some treatments listed hereinafter.

MENDING THIN PAPER OBJECTS AND TRACING PAPERS

The first application of nanocellulose films on museum objects was performed on a series of viewing slides from the mid-19th century belonging to the French Museum of Cinema (La Cinémathèque Française). These objects were originally inserted through a show box to be able to watch them under reflected and transmitted light to create daytime, nighttime, and changing scenery effects (Mannoni 1996). These objects are made of two sheets of thin translucent papers. Most of these slides had large tears, which weakened the structure and interfered with the legibility of the images. The main goal of conservation treatment was to increase legibility of the damaged viewing slides under both reflected and transmitted light. Additionally, it was important to respect the process of the inventor and his choice of the transparency of the materials that were used to make the slides. The new conservation method used to treat these objects has been detailed in another publication (Dreyfuss-Deseigne 2017b). Large tears were mended using strips of MFC film and 5% Klucel G in ethanol, and treatment was regularly done on a light table (Stanley 1996) (fig. 6).

Fig. 6. Strips of MFC film are cut and pasted with Klucel G in ethanol (left) to mend large tears on the verso of the viewing slide (center). Viewing slide in transmitted light before and after mending (right).

Fig. 7. Pierre-Henri Amand-Lefort, *Viewing slide of Oxford,* 1850, 14.5 x 20 cm. Reflected light (left) and transmitted light (right), before and after treatment. (La Cinémathèque Française—Dreyfuss-Deseigne)

The results of these treatments are visible in figure 7, which shows a viewing slide in reflected light (left) and in transmitted light (right), before and after treatment with strips of nanocellulose film.[3]

Using the same method, strips of MFC film were used to mend an architectural drawing on tracing paper by the architect Louis Kahn belonging to Architectural Archives of the University of Pennsylvania in Philadelphia. The large tear on this tracing paper was mended using strips of MFC film and a 5% Klucel G in ethanol (fig. 8).

MENDING GELATIN WINDOWS

Some of the viewing slides belonging to the French Museum of Cinema have gelatin windows at the verso that were used to increase the visual effects while the slides were viewed under transmitted light. But some of these gelatin windows had large cracks, which were consolidated using strips of MFC films. The results are visible in figure 9.

CONSOLIDATION OF ANIMATION CELS

Nanocellulose films were also used in the conservation treatment of animation cels that had been used for production of the cartoon *Jeannot l'intrépide* from the animation director Jean Image in the 1950s, from the French National Center of Cinematography (Centre National de la Cinématographie). These objects are hand painted on transparent sheets of cellulose acetate. A major and recurrent problem of these objects is delamination of the media after aging of the cellulose acetate sheet. Some tests were performed to consolidate the media. CNC film was selected for this treatment, as this material is as transparent as the cellulose acetate sheet, and the same method of application described with MFC film was used. As is visible in figure 10, some fragments of the media were readhered to the support using strips of CNC films and Aquazol 200. This method also gives a new support to the paint in these treated areas.

CONCLUSION: NEW AND PROMISING MATERIALS FOR CONSERVATION PROFESSIONALS

The field of nanotechnology offers many new possibilities to the field of art conservation. Nanotechnologies allow conservators to work with new materials offering unique and innovative properties and to acquire new methods with many advantages. The use of nanocellulose film already proved to be the most effective solution for some specific problems experienced with museum objects. This study was an opportunity to gather new information about the material, such as its reaction to different aging tests and its behavior while combined with adhesives generally used in paper conservation.

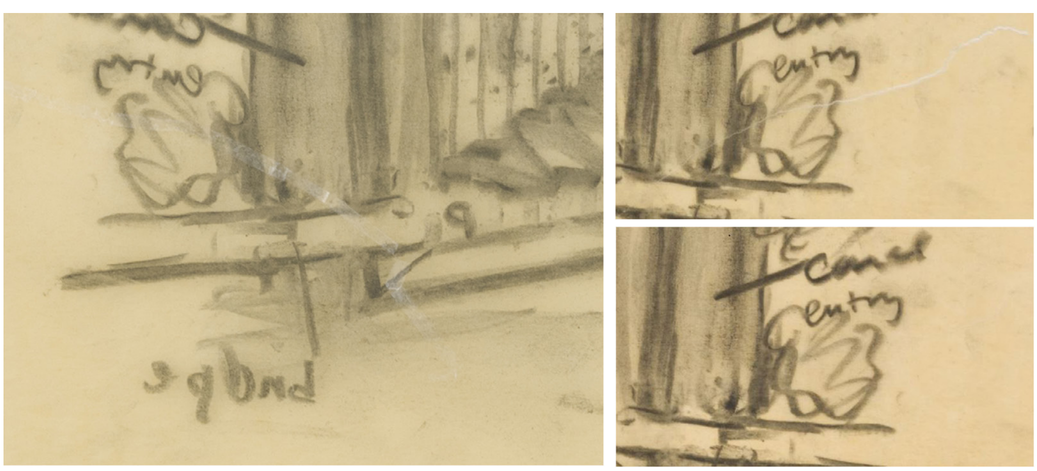

Fig. 8. Louis Kahn, *FDR Memorial in NYC*, 1973, charcoal on tracing paper, 30 x 43 cm, University of Pennsylvania Architectural Archives. Detail of a large tear mended on the verso with strips of MFC film (left) and detail of the recto before and after treatment (right). (CCAHA)

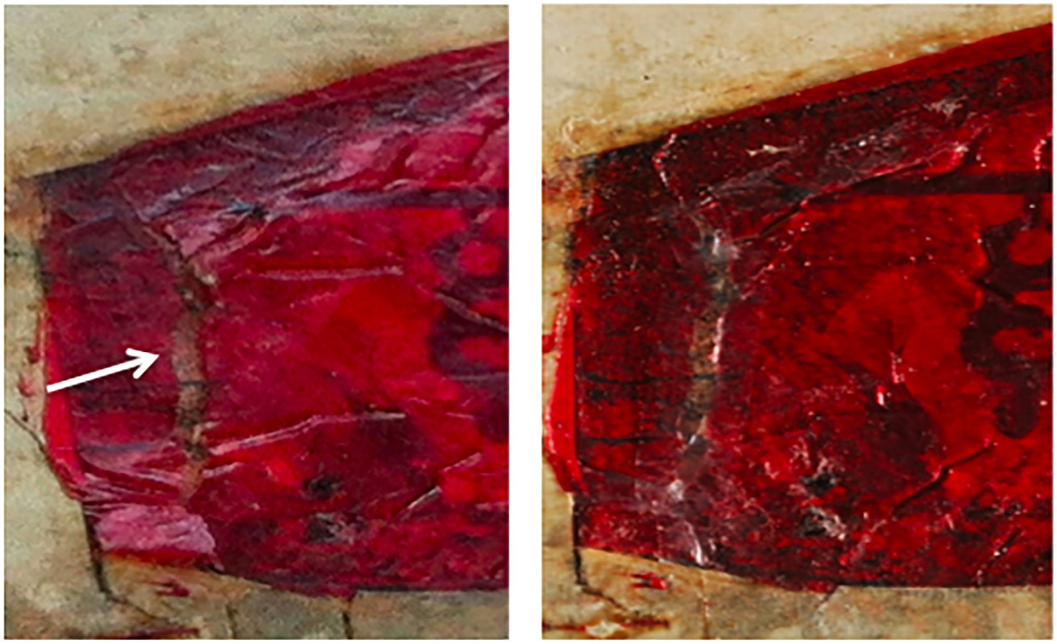

Fig. 9. Gelatin window visible on the verso of one of the viewing slides from the series with a large crack (left) and consolidated with strips of MFC film (right). (La Cinémathèque Française—Dreyfuss-Deseigne)

After having used this material for the first time on museum objects, it is now clear that nanocellulose film is a very promising material. MFC film could be a perfect solution to other problems visible on a wide range of media, such as graphic, photographic, and cinematographic artworks and documents, old or contemporary, made of translucent or transparent supports. The use of nanocellulose films in the field of paper or film conservation today is a fairly new field of investigation. A new research project is currently being carried out at the Research Center for Conservation (CRCC, Paris, France) to further characterize these materials and to study their new possible applications in art conservation. It entails a partnership with American and French nanocellulose manufacturing laboratories, the French Museum of Cinema, and the French National Center of Cinematography. The study is also a good opportunity to work closely with some nanocellulose manufacturers to develop these new and promising materials specifically for conservation professionals.

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Fig. 10. Jean Image, *Jeannot l'intrépide*, 1950, ink and gouache on cellulose acetate, French National Center for Cinematography, Tetras Quebec Inc. Detail showing delamination of the media (left) and consolidation with strips of CNC films (center and right). (CNC—Dreyfuss-Deseigne)

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NOTES

1. This method, invented and developed by Albin F. Turbak, Fred W. Snyder, and Karen R. Sandberd, is presented in US Patent 4378381A: *Suspensions containing microfibrillated cellulose* (published October 1980; registered March 1983).
2. During the drying of the MFC solution under temperature and humidity control, it is advised to put a lid on the petri dish, covering part of it, to make a very homogeneous film and to avoid any dispersion of the microfibrils in suspension. The use of deionized water also avoids any lime scale residues at the surface of the film once dried.
3. Mending viewing slides with large tears required the removal of the secondary support to gain access to the verso of the primary support. Removal was undertaken following a technique described by Ted Stanley, senior paper conservator at the Firestone Library of Princeton University, who worked on similar objects in the 1990s (Stanley 1996). The secondary support was removed from the primary using pieces of blotters dampened with deionized water heated with a tacking iron through a piece of nonwoven polyester. After removal, the two sheets (the primary and the secondary supports) were treated independently and mended with strips of MFC film. The two supports were then realigned again, following the exact original alignment.

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