Journal of Cultural Heritage xxx (2016) xxx–xxx

Available online at
ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en

Short note

Cellulose nanocrystal-based composite for restoration of lacunae on damaged documents and artworks on paper

Camilla H.M. Camargos[a], João C.D. Figueiredo Junior[b,*], Fabiano V. Pereira[a]

[a] Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Belo Horizonte 31270-901, Minas Gerais, Brazil
[b] Departamento de Artes Plásticas, Escola de Belas Artes, Universidade Federal de Minas Gerais, Belo Horizonte 31270-901, Minas Gerais, Brazil

ARTICLE INFO

Article history:
Received 23 May 2016
Accepted 13 October 2016
Available online xxx

Keywords:
Cellulose nanocrystal
Paper restoration
Mechanical testing
Infrared spectroscopy
Scanning electron microscopy

ABSTRACT

Cellulose nanocrystals are a potentially useful material for filling lacunae of documents and artworks on paper due to their high chemical stability and specific physical properties. A composite of cellulose nanocrystals with propylene glycol, methylcellulose and $CaCO_3$ was obtained. Chemical and physical properties of the cellulose nanocrystal-based were compared with properties of conventional papers. Samples were tested by pH measurements, infrared spectroscopy, stress–strain testing, and scanning electron microscopy. Crystallinity index of the cellulose nanocrystal-based composite paper was about three times higher than that of the reference conventional paper. Nanocrystal-based composite and conventional papers presented similarity in stress–strain behavior. The results make nanocrystal-based composite a candidate for reintegration of lacunae of documents and artworks on paper.

1. Introduction

A large amount of cultural heritage collections are composed by paper-based artifacts, such as painting, drawing, engraving, print, watercolor, rare books, documents, manuscripts, photographs, and maps. It is estimated that libraries and archives worldwide currently store approximately 2.5 million km of works on paper [1]. Therefore, it is a relevant ubiquitous medium that has aroused interest in the field of art preservation and restoration.

Paper is composed of many compounds and cellulose is its most important structural component. Pathologies are usual in paper deterioration such as depolymerization by acid hydrolysis of cellulose, photooxidation. Among all of these pathologies, the emergence of lacunae (gaps or holes) can be cited here, in particular. Paper partial losses affect the painting, drawing, engraving, and printing as well as the strength of the artifact. Consequently, conservation and restoration interventions are usually required.

A technique usually applied to treat lacunae is reintegration which consists of the operation of restoring the object entirety by filling the missing areas with strips or patches of new paper, also called grafts; these grafts fit thoroughly into the lacunae. Besides its esthetic relevance, this procedure is important to interrupt the increase in the gaps and minimize future structural damages, ensuring the conservation of the cultural heritage [2,3].

In an effort to provide a suitable solution related to the filling of lacunae on paper by manual reintegration, we studied an alternative material to fill lacunae. This material is composed of cellulose nanocrystals (CNC). There are two major structural zones within cellulose: amorphous and crystalline. Amorphous regions show disarrangements and chains alignment failures, which create space for reagents, making it more prone to acid attack and kinetically more susceptible for deterioration reactions. Crystalline domains in which chains are highly ordered are more chemically stable due to the absence of spaces where chemicals can react. CNC are obtained from the crystalline domains and they are rod-like or whisker shaped particles that can be extracted from cellulose through hydrolytic processing of fibers [4]. CNC have high crystallinity index and are a promising nanomaterial with great stability and versatility.

2. Research aims

This work aims at achieving a novel CNC-based paper pulp as an alternative material in the filling of lacunae of documents and artworks on paper. Aqueous dispersion of CNC, $CaCO_3$ (filler), propylene glycol (plasticizer), and methylcellulose (sizing agent) are the components of the developed paper pulp. Due to its mechanical properties and chemical compatibility with paper, it is potentially useful to aid the restoration of paper artifacts.

---

* Corresponding author. Tel.: +55 31 99213 0441.
E-mail address: joaoc@ufmg.br (J.C.D. Figueiredo Junior).

http://dx.doi.org/10.1016/j.culher.2016.10.007
1296-2074/

Please cite this article in press as: C.H.M. Camargos, et al., Cellulose nanocrystal-based composite for restoration of lacunae on damaged documents and artworks on paper, Journal of Cultural Heritage (2016), http://dx.doi.org/10.1016/j.culher.2016.10.007

3. Experimental

3.1. Materials

Propylene glycol (Labsynth) and methyl cellulose (Sigma–Aldrich) were used without further purification. Calcium carbonate was synthetized by reacting calcium chloride and sodium carbonate (analytical-grade reagents). Cellulose fibers were provided from reprocessed papers: Hahnemühle Ingres white paper (50%) and Canson Mi-Teintes Board (50%). Two wood cellulose paper sheets from a book printed in 20th century were used for simulated reintegration.

3.2. Preparation of cellulose nanocrystals

CNC were extracted by processing eucalyptus fibers, which were milled, submitted to alkali and bleaching treatments with $NaOH/NaClO_2$, and then hydrolyzed with H_2SO_4. Finally, the system passed through dialysis process in aqueous medium (semipermeable membranes were employed) and CNC were obtained [5].

3.3. Preparation of CNC-based paper samples

Four relevant components were concerned in several contrasting rates to elaborate the CNC-based paper pulp (Table 1). CNC pulp was prepared by combining the above-mentioned compounds in aqueous medium and then submitting the slurry to sonication for 2 min (750 W, 20 kHz). In plastic Petri dish, the homogeneous suspension was dried at normal temperature and pressure (NTP). After 48 h, water evaporated and sample paper sheet was obtained.

Preliminary organoleptic evaluations of samples were conducted by considering the following specific parameters: opacity, flexibility, tear strength, folding endurance, and corrugation aspect. By means of this assessment, it was observed that the effectiveness of the optical and mechanical properties was the best in formulation 8. The obtained composite sample presented high opacity, satisfactory mechanical performance (flexibility, tear strength, and folding endurance) and did not show any representative surface corrugation.

3.4. Preparation of reprocessed cellulose fibers-based paper samples

Two fundamental constituents were employed to obtain reprocessed cellulose fibers-based paper pulp: cellulosic fibers, provided from reprocessed pulp (aqueous suspension composed of 1.26 g solid pulp per 100 mL H_2O); and methylcellulose (12 wt%). Fluid pulp was prepared by blending the compounds under mechanical agitation. In a plastic Petri dish, the homogeneous slurry was dried at NTP. After 48 h, the solvent evaporated and the sample paper sheet was prepared (total mass: 300 mg).

3.5. Simulated reintegration applying CNC and cellulose fibers-based paper pulps

Both wood cellulose paper sheets employed in the simulated applications were provided with lacunae: a cut elliptic hole (maximum axis: 4 cm) and small insect gaps. The reintegration was processed with punctilios insertions of pulp slurry by using a glass dropper. Reprocessed cellulose fibers-based pulp applying method was developed upon a blotting paper board, and filled areas were pressed under a nonwoven fabric sheet using a Teflon® spatula. At NTP, the material dried in 24 h. CNC-based pulp filling method was performed upon an acrylic plastic sheet, and a demand, to repeat the grafting for three to five times until the thickness of the restored paper matched, was placed. At NTP, each composite layer required 30–120 min to dry.

3.6. Analysis and testing methods

Surface pH measurements were made with pH-indicator paper strips (Merck Millipore, pH range: 0 to 14, non-bleeding type). A polyester film was placed beneath the paper sample. Small amount of water was applied with a dropper to the area to be tested. The strip face was pressed down into the wetted zone. After 1 min, the strip was removed and the pH was recorded [6,7].

Fourier Transform Infrared Spectra (FTIR) were collected with a 4 cm^{-1} resolution using a Bomem MB100 FTIR.

Scanning Electron Microscopy (SEM) images were obtained with a FIB–Quanta FEG 3D FEI electron microscope. Paper samples were coated with a thin layer of gold [8].

Tensile testing was performed with standard tensile specimens (rectangular cross section, useful part: 20 mm). Samples, settled in an ambient environment of 21 °C (± 5 °C) and a relative humidity (RH) of 55% (± 5%) [9], were mounted by the end and into the holding grips of the testing apparatus (LR 5 K machine, furnished by Lloyd Instruments, with a 10 N load cell and constant elongation rate of 3 mm/min). Tests were done in triplicate.

Visual examinations of reintegrated paper sheets were performed with frontal fluorescent light, raking fluorescent light and long wave ultraviolet fluorescent light [10]. NIKON D60 camera (55 mm lens reflex) was employed. GretagMacbeth™ ColorChecker Color Rendition Chart aided to preserve authentic colors information of the recorded objects.

Table 1
Formulations of CNC-based paper pulp and preliminary aspects of obtained paper samples.

Samples	CNC (wt%)	$CaCO_3$ (wt%)	Propylene glycol (wt%)	Methylcellulose (wt%)	Organoleptic aspect of obtained paper
1	44	12	44	0	High opacity. Low flexibility. Low tear strength. No folding endurance. High corrugation
2	45	10	45	0	High opacity. Regular flexibility. Low tear strength. No folding endurance. High corrugation
3	46	8	46	0	Regular opacity. Regular flexibility. Low tear strength. No folding endurance. High corrugation
4	48	4	48	0	Low opacity. Regular flexibility. Low tear strength. No folding endurance. High corrugation
5	48	10	42	0	High opacity. Low flexibility. Low tear strength. No folding endurance. High corrugation
6	49	2	49	0	Low opacity. Regular flexibility. Low tear strength. No folding endurance. High corrugation
7	58	10	32	0	High opacity. Regular flexibility. Low tear strength. No folding endurance. Regular corrugation
8	66	10	12	12	High opacity. High flexibility. High tear strength. Folding endurance. Without corrugation
9	68	10	0	22	High opacity. High flexibility. High tear strength. Folding endurance. High corrugation
10	68	10	22	0	High opacity. High flexibility. Regular tear strength. No folding endurance. Low corrugation
11	68	10	8	14	High opacity. High flexibility. High tear strength. Folding endurance. High corrugation
12	78	10	12	0	High opacity. High flexibility. Low tear strength. No folding endurance. Regular corrugation
13	88	10	2	0	High opacity. Regular flexibility. Low tear strength. No folding endurance. Regular corrugation

Please cite this article in press as: C.H.M. Camargos, et al., Cellulose nanocrystal-based composite for restoration of lacunae on damaged documents and artworks on paper, Journal of Cultural Heritage (2016), http://dx.doi.org/10.1016/j.culher.2016.10.007