



A new smart material constituted of *Funori* and Ca(OH)₂ nanocrystals: Implications in cultural heritage conservation

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ABSTRACT

An innovative material constituted of a natural biopolymers blend (*Funori*) from *Gloiopeltis* algae and Ca(OH)₂ nanocrystals was developed to consolidate linen fibers for cultural heritage conservation preventing future degradation due to the alkaline reservoir by Ca(OH)₂. The procedure to extract *Funori* from the algae was reliable and reproducible and the consolidation performances for aged linen fibers of the *Funori*/Ca(OH)₂ nanocrystals smart system were showed highly promising in cultural heritage conservation.

1. Introduction

Funori is a blend of biopolymers – mainly polysaccharides – extracted from *Gloiopeltis* algae [1,2] used for many applicative purposes [3–5]. A very interesting use of *Funori* is in the field of cultural heritage conservation: it is considered a good consolidant and adhesive for the conservation of works made of cellulose (paper, linen, cotton) [4,6,7]. Consolidation of works made of cellulose like linen textiles is often needed due to the loss of mechanical properties attributed to cellulose depolymerisation, also associated to acidification processes [8]. At present two main problems remain open: (i) set-up of a reproducible, well characterised procedure to obtain *Funori*, to avoid undesirable effects due to not controlled material preparation, and (ii) the need of adding to *Funori* a material able to prevent degradation. This study was aimed to develop a new smart material constituted of a well characterised and unique *Funori* loaded with Ca(OH)₂ nanocrystals [9]. The goal was to combine the consolidation of *Funori* with the preventive conservation by Ca(OH)₂ nanocrystals as alkaline reservoir to buffer future acidification processes which enhance cellulose depolymerisation.

2. Experimental

0.80 g of the *Gloiopeltis* alga were mixed with 79.2 g of Milli-Q water

and the heterogeneous system, under magnetic stirring, was kept for 2.5 h at 30 °C (sealed vessel) or 60 °C (open vessel heated to reflux). Then the heterogeneous system was immediately filtered without cooling by a steel strainer with 1 mm mesh size. The liquid part was centrifuged, and the supernatant fraction was evaporated by a rotavapor from 80.0 mL to 15–20 mL. The concentrated solution was frozen in liquid nitrogen and lyophilised at 50–80 mbar for 72 h. The new smart system was obtained applying onto the aged linen yarns (by brushing) the above obtained *Funori* dispersed in water 1 % (w/w) with or without the preliminary application of a Ca(OH)₂ nanocrystals dispersion in 1-propanol 5 g/L.) [9]. Other details for this section are reported in a Supplemental File.

3. Results and discussion

The extraction of *Funori* gave a yield about 35 %, independently on the temperature. Even if the use of higher temperatures (60 °C) favoured the initial solubilisation of greater quantities of alga, the work up at room temperature determined a final yield like that obtained at 30 °C. The ATR-FTIR spectra were very similar for both extraction temperatures and the peaks matched those reported for carrageenan [10,11] and agar [12,13] components. It was interesting that the polysaccharide fraction contained both anhydrous and sulphurated galactose units. The presence of sulphurated galactose units was deducible from the absorption at 1,222 cm⁻¹ (O=S=O asymmetric stretching on the C₆

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Table 1

Band intensity *I* (arbitrary units) and band area *A* (arbitrary units) at 933, 1,064, and 1,222 cm^{-1} as a function of the extraction temperature.

$[I(1,222 \text{ cm}^{-1})/I(1,064 \text{ cm}^{-1})]_{60^\circ\text{C}} - [I(1,222 \text{ cm}^{-1})/I(1,064 \text{ cm}^{-1})]_{30^\circ\text{C}}$	-0.089
$[A(1,222 \text{ cm}^{-1})/A(1,064 \text{ cm}^{-1})]_{60^\circ\text{C}} - [A(1,222 \text{ cm}^{-1})/A(1,064 \text{ cm}^{-1})]_{30^\circ\text{C}}$	-0.149
$[I(933 \text{ cm}^{-1})/I(1,064 \text{ cm}^{-1})]_{60^\circ\text{C}} - [I(933 \text{ cm}^{-1})/I(1,064 \text{ cm}^{-1})]_{30^\circ\text{C}}$	+0.044
$[A(933 \text{ cm}^{-1})/A(1,064 \text{ cm}^{-1})]_{60^\circ\text{C}} - [A(933 \text{ cm}^{-1})/A(1,064 \text{ cm}^{-1})]_{30^\circ\text{C}}$	+0.028

Table 2

TGA data for all the samples analysed. T ($^\circ\text{C}$) refers to the centre of the weight decrease curve.

Extraction T ($^\circ\text{C}$)	RH (%)	T ($^\circ\text{C}$)	Weight decrease (%)
30	32.8	50.6	15.1
	45.0	50.1	18.2
	57.6	48.9	19.8
	75.3	49.2	28.2
	100	62.1	77.6
60	32.8	56.8	14.3
	45.0	52.6	17.4
	57.6	51.8	18.4
	75.3	47.9	26.3
	100	55.7	77.9

position) [10–12]. Since there were no differences between the signals in the spectra of the fractions extracted at 30 and 60 $^\circ\text{C}$, we focused on the quantitative composition analysing the intensity and area of the two absorptions characteristic of the polysaccharide versus protein components (1,064 versus 1,558 cm^{-1}), but no significant results were found, indicating no meaningful difference between the two temperatures. Instead, interesting results were found comparing intensity and area of the following bands: 1,064 cm^{-1} corresponding to all the galactose units (sulphurated, not sulphurated, anhydrous and hydrated), 1,222 cm^{-1} corresponding to only sulphurated units, and 933 cm^{-1} attributed to the stretching of the $\text{C}_3 - \text{O} - \text{C}_6$ of the anhydrous structures overlapped with the bending of the $\text{C} - \text{H}_1$ of units in the anomeric form (the α -structures are all 3,6-anhydrous- α -galactose) [10–13]. Table 1 reports the changes detected in passing from 30 to 60 $^\circ\text{C}$. The temperature increase favoured the extraction of polymers with a higher content of anhydrous galactose

units (agar-like structure) with respect to those with high content of sulphurated chains (carrageenan-like structures). The ^1H - and ^{13}C NMR spectra were interpreted considering the data in the literature [14–17] and they confirmed ATR-FTIR findings, that is the temperature did not lead to a significant change of the biopolymer composition of the blend, apart from a slight decrease of the sulphurated chains content with a corresponding increase of the anhydrous ones when passing from 30 to 60 $^\circ\text{C}$.

The interaction between water vapour and *Funori* was investigated studying the water vapour desorption, after a previous treatment at various Relative Humidity (RH). Table 2 summarises the results obtained by Thermo-Gravimetric Analysis (TGA) that show that the weight decrease, due to the desorption of the water bound to the biopolymers' chains (detected by ATR-FTIR) occurred around 50–60 $^\circ\text{C}$. From the data reported in Table 2 it was possible to deduce that the amount of desorbed water (% weight decrease in Table 2) increased as a function the pre-treatment RH-values, but not linearly, with a strong jump in passing from treatment at RH = 75.3 % up to at RH = 100 %. This drastic increase showed the presence of a critical saturated vapour pressure at 75.3 % < RH \leq 100 %, that determined a strong biopolymer swelling due to water vapour absorption. This result suggested that the best RH-values to keep works of art treated by *Funori* were in the range 50–60 % where the water vapour absorption is small.

Differential Scanning Calorimetry (DSC) measurements were carried out to estimate the Free Water (FWI), Freezable Bound Water (FBWI), and Not-Freezable Bound Water (NFBWI) Indices according to the literature [18] and comparing them with the weight decrease by TGA. Only the samples maintained at RH = 100 % exhibited a peak typical of water melting slightly below zero (Fig. 1).

For the other samples no peaks were detected, demonstrating that when the treatment was done at RH \leq 75 % the absorbed of water was only not-freezable bound, i.e. all the absorbed water molecules were strongly bound to the polymer chains. For the samples maintained at RH = 100 % for 746 hrs the FWI (%) was calculated according to the literature [18] and the results matched those found by TGA (see Table 2). To test the new smart materials for applicative purposes in textiles conservation, aged linen yarns were treated as reported in Supplemental File using *Funori* with or without $\text{Ca}(\text{OH})_2$ NanoParticles

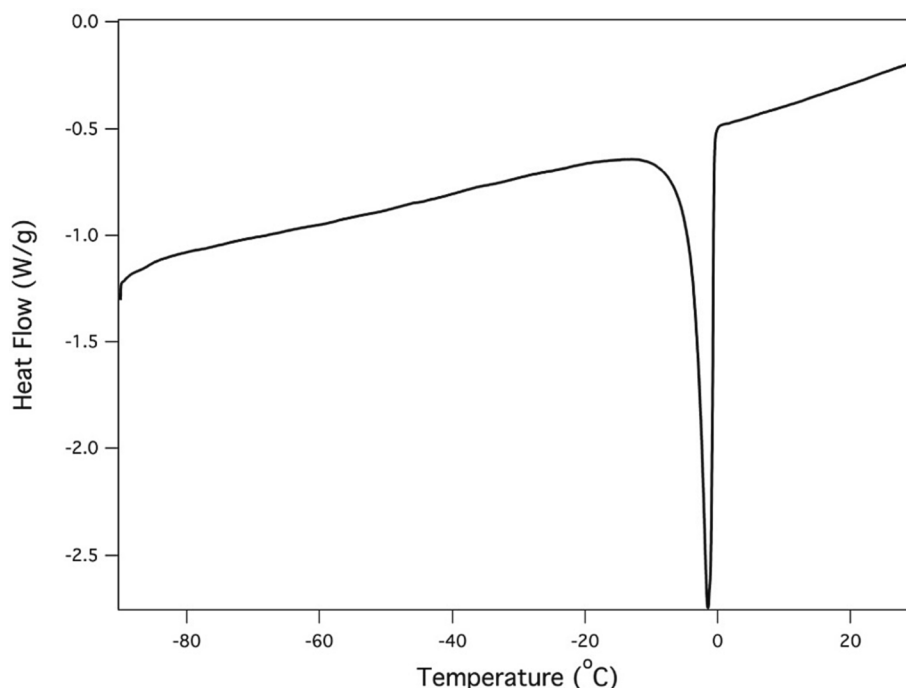


Fig. 1. DSC curve of the *Funori* sample extracted at 30 $^\circ\text{C}$ and cured for 746 h at RH = 100 %.

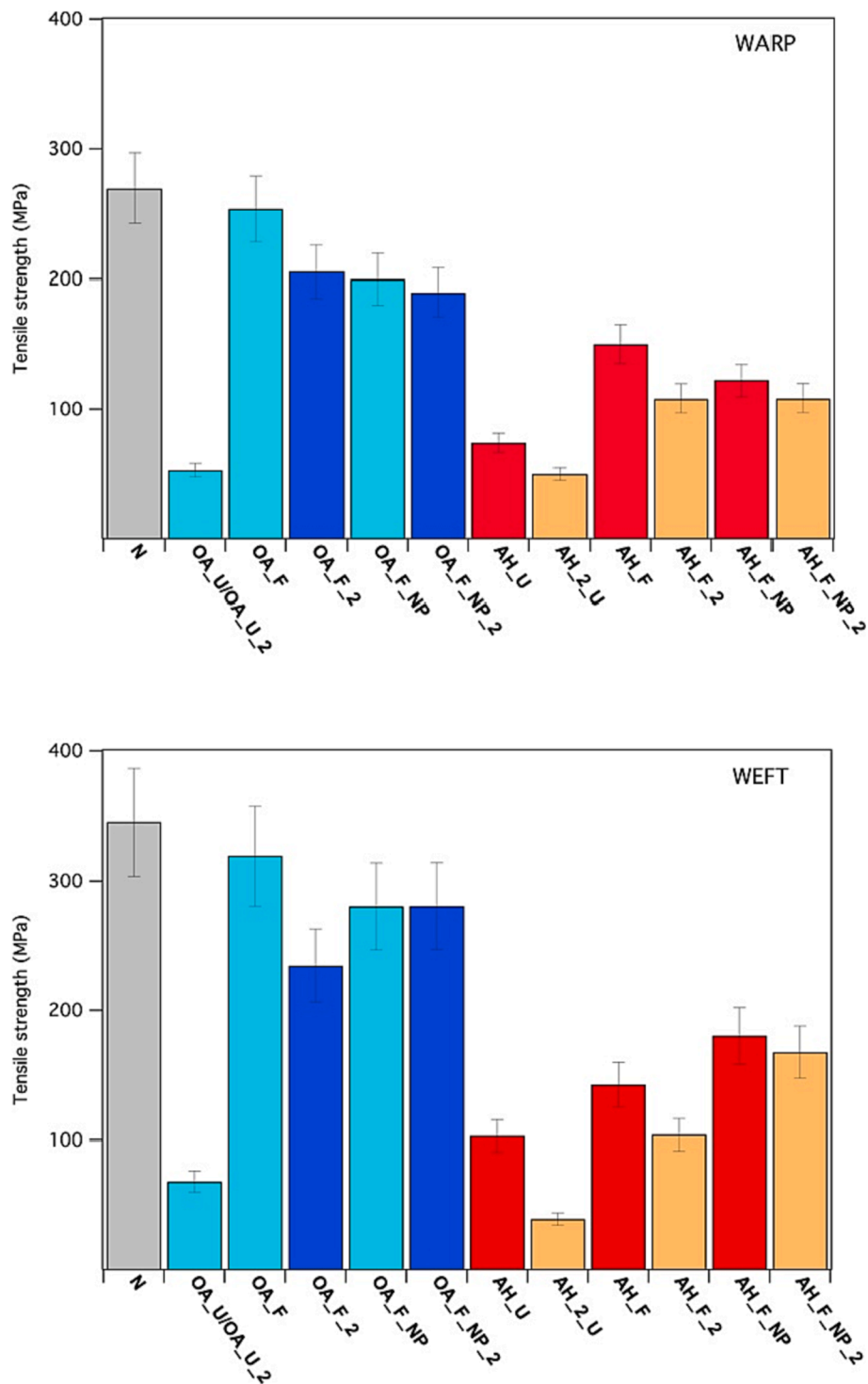


Fig. 2. Tensile strength (MPa) of the linen warp (top) and weft (bottom) aged by the two methods reported in the Materials and Methods section (AH and OA) not treated and treated by different consolidant materials. Meaning of the acronyms: N = not aged, AH and OA refer to the aging procedure; U = Untreated, F = *Funori*, F_NP = *Funori* plus Ca(OH)₂ NanoParticles. 2 indicates the second AH or OA aging treatment.

and tensile strength measurements were carried out according to the procedure reported in the Supplemental File. Fig. 2 shows the behaviour of the tensile strength (MPa) for the linen fibers as a function of both treatments and aging methods.

All the samples consolidated showed increase of tensile strength. The best performance was achieved for samples aged only by acidic treatment (OA): this agreed with the observed decrease of polymerisation degree, that changed from a value of 2,767 to 2,160 (OA aging) and to

634 (AH aging) – for details see Supplemental File. Other interesting results emerged: (i) *Funori* alone and with Ca(OH)₂ nanoparticles had optimum performance as consolidant for OA aged samples and acceptable for AH aged ones, (ii) Ca(OH)₂ succeeded in preventing future deterioration due to the second aging treatment. It was evidenced an unexpected result, that is the addition of an inorganic compound [Ca(OH)₂] to the biopolymer *Funori* resulted in comparable and, in one case, better consolidating performance. This can be promising for further

investigations: the addition of Ca(OH)_2 nanocrystals to *Funori* keeping its consolidating performance opens stimulating perspectives, since Ca(OH)_2 acted as a preventive conservation tool inhibiting acidification processes that lead to cellulose depolymerisation and loss of mechanical properties.

4. Conclusions

An extraction procedure to obtain in a reproducible and reliable way *Funori* from the *Gloiopeltis* algae was developed showing that the temperature did not severely alter the properties of the obtained biopolymers. The extraction at 30 °C favoured the formation of sulphurated chains, whereas at 60 °C the anhydrous galactose units prevailed. TGA and DSC measurements showed an interesting behaviour concerning the interaction between the water vapour and the *Funori* biopolymers establishing the better RH conditions. The consolidating power of the new system constituted of *Funori* and Ca(OH)_2 nanoparticles showed optimum performance, disclosing stimulating perspectives in the field of preventive conservation since the innovative smart composite material simultaneously consolidated and prevented degradation.

CRediT authorship contribution statement

Luigi Dei: Conceptualization, Supervision, Writing – original draft, Writing – review & editing. **Antonella Salvini:** Conceptualization, Supervision, Writing – review & editing. **Benedetto Pizzo:** Conceptualization, Supervision, Writing – original draft. **Emiliano Carretti:** Conceptualization, Data curation, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2022.133558>.

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