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Polymer-coated Nanolimes Dispersions for Reduction, Deacidification and Consolidation of Ancient Paper

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Nanolimes have been widely explored as nanomaterial for cultural heritage preservation. In particular, they have shown interesting properties to contrast the ageing of manuscripts, books and artistic works, opening up the possibility to store such items in a good quality state for longer. In the present work we reported an innovative nanolime-based formulation for paper restoration, which includes in its composition a reducing agent and a fibers consolidator as well. To formulate an efficient product, we deeply investigated the cellulose oxidation process with a multi-technique approach. The here presented formulation consists in a hydroalcoholic ternary dispersion of nanolimes coated with hydroxypropyl methylcellulose (HPMC) and tert-butylamine borane complex (TBAB) as cellulose fibers consolidator and reducer, respectively. The effectiveness of the ternary mixture has been demonstrated on oxidized paper, whose chemical and mechanical properties were partially recovered after the treatment.

1. Introduction

Since the 2nd century AD, paper has been identified as a fundamental material for manuscripts, books and artistic works realization (Erhardt and Tumosa, 2005).
On the chemical point of view, paper is mainly constituted by cellulose, a high molecular weight linear polymer composed of D-glucopyranose units linked by ² -1,4-glycosidic bonds. The cellulose chains arrange in the paper structure to form microscale fibers, whose chemical and physical properties determine the its macroscopic feature. In particular, cellulose hydroxyl groups are involved in several intra- and intermolecular hydrogen bonds, leading to four different crystalline arrangements, namely cellulose I, II, III and IV, among which the allophorm I is the most abundant in nature (Park *et al.*, 2010).
As a biological polysaccharide, cellulose is considered as a green material, since it is extracted from natural sources, e.g. tree wood and other vegetable structures (Chen *et al.*, 2011), it is biodegradable and not hazardous for human healthcare. Nonetheless, some cellulose processing steps widely employed for paper production or preservation involve toxic and, at the industrial scale, big amount of chemicals. Focusing on the paper conservation, restorers currently carry out multi-steps protocols to obtain paper bleaching, deacidification and fibers consolidation, in order to slow the aging effects and preserve precious paper-based cultural heritages (Zervos and Alexopoulou, 2015). Each step can involve liter-scale amount of solutions, often prepared in organic solvents, i.e. alcohols are widely used in this context, and the whole protocol result to be time-consuming. In this context, calcium hydroxides nanoparticles, often referred as nanolimes, have standed out for their interesting properties as functional and advantageous nanomaterial in the cultural heritage field. Applications for the restoration of wall paintings, surface coatings, canvas and paper artworks have been reported, highlighting the great potentialities of nanolimes suspensions as deacidifying agents (Baglioni, Chelazzi and Giorgi, 2014). An advantage of using a nanomaterial respect to the corresponding salt solution is the possibility to tune the particle size in order to control the extent of particles penetration into the porous

matrices and their accumulation as white hazes over the treated artwork surface. Focusing on nanolimes application for precious paper treatment, different colloidal suspensions have been demonstrated to be suitable for paper restoration. In fact, nanolimes formulations are currently on the market and widely applied in the common restorers protocols (e.g. Nanorestore® products). The physisorption of nanolimes on paper sheets results firstly on the deacidification of the artifact, and secondly on a functional alkaline reservoir which avoids further pH decrease (Bastone *et al.*, 2017). However, during the paper restoration process, it is fundamental to take into account that the deacidification step cannot be carried out on a cellulose substrate oxidized in a large extent. Indeed, a large amount of carbonyl groups in the cellulose structure induces an alkali catalysed β-alkoxy elimination reaction, resulting into cellulose degradation and depolymerization (Bicchieri, Bella and Semetilli, 1999). For this reason, a previous step aimed to reduce the carbonyls to hydroxyl groups is mandatory. Tert-butylamine borane complex (TBAB) is among the most widely used compounds in the general practice of paper restoration as chemical reducing agent. Binary formulations consisting in a combination alkaline nanoparticles with molecular reducing agents have been investigated and showed promising results on aged samples of paper (Bicchieri and Sodo, 2016).
The present work aims to show a three components formulation made of nanolime particles suspended in a hydroalcoholic solution of TBAB and hydroxypropyl methylcellulose (HPMC). HMPC is a cellulose derivative added in the nanoformulation to be physisorbed on the cellulose fibers of the paper-based artifacts, in order to partially reconstitute the fibers structure. Then, the ternary nanolime formulation can induce deacidification, reduction and fiber reinforcement of the restored paper in a single treatment, as well as constitute a protective alkaline reserve which limits spontaneously acidification and depolymerization of cellulose. Therefore, the herein described innovative nanolime colloidal suspension can be envisaged as a useful single-step and greener formulation for paper restoration, as can offer the advantages to being less time-consuming and to involving a lower amount of organic solvent for ancient paper treatments.

2. Materials and Methods

Materials. Potassium periodate, 2,3,5-triphenyl-tetrazolium chloride (TTC), potassium hydroxide, hydrochloric acid, tert-butylamine borane complex (TBAB), hydroxypropyl methylcellulose (HPMC), ethanol, isopropanol were all purcheased by Sigma Aldrich. Whatman® n.1 filter paper was used as model cellulose substrate for the oxidation process. Nanorestore Plus® 5 % w/v in isopropanol was supplied by CSGI. All aqueous solutions were prepared in deionized water (d 1µS).
Paper oxidation and analysis. Samples of Whatman® paper were oxidized by immersion in aqueous KIO_4 15 mM (50 mL / 0.5 g of paper) for different times. Then, the samples were washed and dried at room temperature overnight. The carbonyl content in each sample was determined by the TTC assay as reported (Strli• and Pihlar, 1997): 25 mg of paper were soaked in 500 µL of TTC 0.2 % w/v adding 500 µL of KOH 0.2 M to activate the redox reaction. After 10 min at 78 °C, the reaction was stopped by adding 200 µL of HCl 1 M and lowering the bath temperature at ~ 10 °C. The mixtures were diluted to 10 mL with ethanol to solubilize TTF. The absorbance of the resulting red solutions was measured by a UV-Vis spectrophotometer (DU800, Beckman). The carbonyl content was calculated from the absorbance value at 482 nm through a calibration curve obtained by using glucose standard solutions.
After the oxidation process, the paper samples were analyzed by X-ray diffraction (XRD) with Bruker D8 Advance diffractometer, using a Co source, voltage 40 kV and current 25 mA in the 2¸ range of 5-70°. The ATR FT-IR spectra of some samples were acquired by using a Bruker Vertex 70v spectrophotometer with platinum ATR, resolution of 2 cm^{-1} and 200 scans in the acquisition range 4000–70 cm^{-1} at 2 hPa.
Ternary system formulation and application. The ternary Nanolimes formulation was prepared as a colloidal suspension containing Nanolimes 0.05 % w/w, TBAB 0.875 % w/w and HPMC 0.1 % w/w in 9:1 isopropanol/water. Paper samples oxidized for 48 h were treated with the ternary formulation by immersion for 24 h then dried at room temperate overnight without any washing. Mechanical properties of treated samples (10 mm × 90 mm) were evaluated by using a dynamometer Instron 3365 equipped with a 1 kN cell. In all cases, the crosshead speed of 1 mm/min was set for the first 2 min, then 50 mm/min until the breaking. The slope of the stress-strain curve was used to extrapolate the elastic modulus (E) value at zero. The stress at the break (Ã) and elongation at break (µ) correspond to the maximum values of the stress and deformation measured during the mechanical tests, respectively.

3. Results and Discussion

3.1. Paper Oxidation

The first step of the present work consisted in a deep investigation of the cellulose oxidation process in order to obtain fundamental information to properly design an effective nanoparticle formulation for paper

restoration. The oxidative process was studied on Whatman® filter paper as model sample of pure cellulose fibers. This substrate was used to simulate the ageing of the paper by means of the oxidation reaction with aqueous KIO_4 (15 mM). The choice of KIO_4 as oxidizing agent was due to the possibility to carry out a selective oxidation on the cellulose chain at the C2-C3 bond of the glucosidic ring. The reaction mechanism is reported in Figure 1, where the formation of a cyclic intermediate is highlighted, which evolves in the C-C bond breaking and hydroxyl groups conversion to carbonyls.

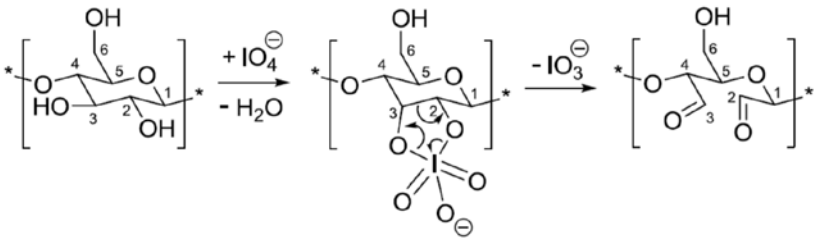

Figure 1. Oxidative mechanism of cellulose by periodate through cyclic intermediate formation.

The oxidation of the paper fibers was firstly quantified by means of a colorimetric assay based on the reduction of 2,3,5-triphenyl-tetrazolium chloride (TTC) to 1,3,5-triphenyl-tetrazolium formazane (TTF) (Strli• and Pihlar, 1997). Such an assay is well-established in cell biology to evaluate cells viability. In fact, if carbonyl groups are present in the cellulose structure, the reduction reaction with TTC turns the color solution into red. This approach enabled to confirm the oxidation of cellulose by KIO_4 and to study the kinetic of the oxidation process, following the reaction by the TTC assay at different times.

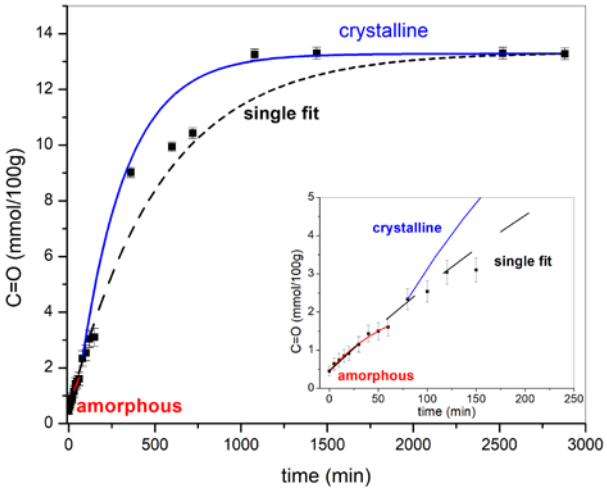

Figure 2. Kinetic of paper oxidation in terms of carbonyl groups content per 100 g of paper. The amount of aldehyde carbonyl groups was quantified by the TTC assay.

The Figure 2 shows the curve obtained following the absorbance variation of TTF at 482 nm. Interestingly, the kinetic of the cellulose oxidation appears a bimodal process. The first step (0-60 minutes, red fit) is thought to mainly consists in the oxidation of the cellulose chains in the amorphous phase, while the second step (60-2880 minutes, blue fit) is ascribed to the oxidation of the crystalline domains (Potthast *et al.*, 2007). In fact, the data analysis using an exponential fit for each step of the kinetic showed a high quality fit respect to a single exponential.
In order to investigate the effects of the paper oxidation in terms of crystallinity variations, which is a fundamental aspect in determining the paper macroscopic properties, the kinetic of oxidation was also studied by XRD and ATR FT-IR. Figure 3 shows the results obtained by the crystallinity investigation.

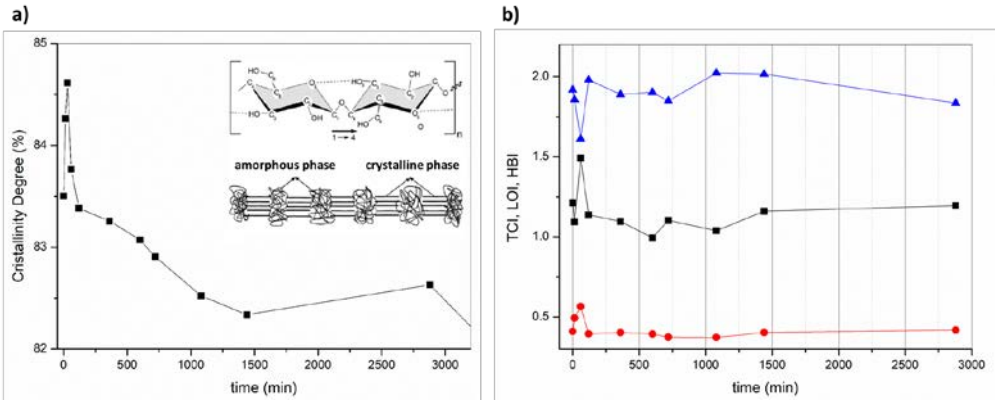

Figure 3. (a) Degree of crystallinity of paper oxidized at different times calculated from the XRD patterns (inset: cellulose chemical structure and phase domain scheme), and (b) LOI (red), TCI (black) and HBI (blue) parameters calculated from ATR FT-IR spectra.

The complex evolution of cellulose crystallinity was also confirmed by XRD and ATR FT-IR data. The XRD pattern of untreated Whatman® paper revealed a crystallinity degree of 83.5 % (Costa *et al.*, 2014), calculated from the peak intensities at 2θ of 22 ° and 27 °, related to the amorphous and crystalline phase, respectively (Sun *et al.*, 2015). For longer oxidation time, an increase in crystallinity was measured up to 84,7 % at 30 min. Then, the crystallinity degree decreases as expected.
Concerning the crystallinity analysis by ATR FT-IR, a bimodal kinetic evolution of paper crystallinity was also observed. In particular, in the present work three of the most widely used parameters for crystallinity semi-quantitative evaluation were calculated from FT-IR spectra: Lateral Order Index (LOI, ratio of 1429/893 peaks), Total Crystallinity Index (TCI, ratio of 1372/2900 peaks), and Hydrogen Bond Index (HBI, ratio of 3332/1336 peaks). They all can be assumed to give information about the amount of crystalline and amorphous phase in a cellulose sample (Široký *et al.*, 2010). Also the analysis of LOI, TCI and HBI parameter as functions of the oxidation time revealed a higher crystallinity degree at 30 min, and a following decrease.

Another important parameter to take into account in the paper analysis and restoration is the pH. In fact, both acidic and alkaline hydrolysis of cellulose can occur at extreme pH values. In figure 4 the pH evolution during the oxidation is shown.

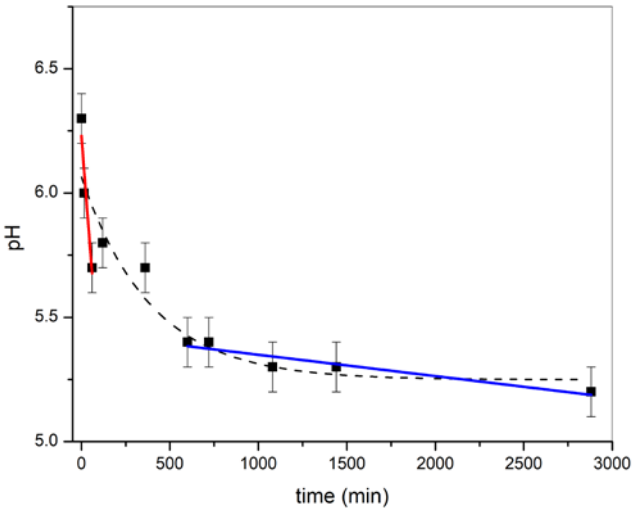

Figure 4. pH values at different oxidation times. The pH decays exponentially (black dashed curve), with a faster pH decrease in the first phase (red line) and a slower variation in the second phase (blue line).

The pH decrease during the oxidation process from 6.6 (untreated paper) to 5.2 (48 hours of oxidation) with an exponential decay till a plateau value. The exponential regime can be seen as resulting from a first phase of fast oxidation, likely associated to the chemical reaction of periodate with the cellulose chains in the amorphous state, followed by a second slower phase of oxidation associated to the chemical modification of the cellulose chains in the crystalline domains. According to the data obtained from the TTC assay, XRD and ATR FT-IR, such a kinetic change is observed after ~ 1 h of oxidation.

3.2 Restoration Treatment

The samples of paper after 48 hours of oxidation with KIO_4 15 mM were treated with the Nanolimes particles suspension, the binary system Nanolimes/TBAB and the ternary system Nanolimes/TBAB/HPMC. The mechanical properties were tested after each step of the process and the results are reported in Table 1.

Table 1. Elastic modulus (E), stress at the breaking point (Ã) and elongation at the breaking point (µ) of paper samples after oxidation and restoration treatments.

Whatman sample	Ē (MPa)	Ã (MPa)	µ̄ (%)
untreated	1,400 ± 8	15.1 ± 0.8	2.3 ± 0.2
48h KIO_4	901 ± 6	6.4 ± 0.4	2.1 ± 0.2
48h KIO_4 + TBAB	938 ± 5	7.4 ± 0.4	2.1 ± 0.1
48h KIO_4 + Nanolimes	1,193 ± 6	15.2 ± 0.6	2.3 ± 0.2
48h KIO_4 + HPMC	655 ± 5	9.0 ± 0.5	2.6 ± 0.2
48h KIO_4 + Nanolimes/TBAB/ HPMC	1,057 ± 5	9.0 ± 0.4	1.8 ± 0.1

In Table 1 the values of elastic modulus (E), stress at the break (Ã) and elongation at break (µ) are reported. As expected the mechanical resistance of the paper after the 48 hours oxidation reaction lowers, resulting in a more fragile material. In fact, the oxidation and likely partial depolymerization of the cellulose chains is expected to damage the paper fibers making the material more susceptible to mechanical stress. The treatments of the oxidized paper with TBAB and HPMC are not sufficient to recover the mechanical properties of the paper, while the treatment with the Nanolimes suspension shows an important consolidation effect. This allows to affirm that the nanoparticles play a crucial role as consolidator as well, likely by physically crosslinking the cellulose chains each others. The ternary system showed a good result in term of recovering of the paper mechanical properties, even if slightly less performant respect to the suspension containing the only Nanolimes. However, the ternary system is advantageous since it offers not only an important recovery of the mechanical properties of the paper substrate, but also the possibility to simultaneously reduce the oxidized carbonyl group, which is an important aspect for bleaching the paper and limiting the further oxidation by ageing.

Conclusion

The multi-technique approach herein applied for the investigation of the paper oxidation process allows to infer a complex mechanism of oxidation for paper-based substrates. The coexistence of amorphous and crystalline phases for the cellulose supramolecular structure leads to a different behavior in terms of chemical reactivity towards the KIO_4 for the two phases. The amorphous phase is characterized by short distance organization lost at longer distances and a high chain mobility that result in higher reactivity. The crystalline phase, made of packed polymeric chains appears as generally more resistant to chemical modifications. This different structure arrangement determines a kinetic of oxidation consisting in two different steps with a regime variation at 1 hour. The crystallinity degree increases up to 1/2-1 hour since the amorphous phase chains are firstly oxidized and likely partially degraded by depolymerization. Then, the oxidation process is characterized by an initial increase of the total amount of the crystalline portion in the sample. As the crystalline domains begin to be oxidized and destructured as well, the crystallinity degree decrease is observed.
Taking into account the physicochemical aspects of the paper oxidation process, as well as the peculiar needs of paper restorers, the herein described Nanolime ternary suspension was designed and successfully applied on Whatman® paper model substrates. The ternary Nanolimes system demonstrated to be a useful mixture to reduce, consolidate and obtain an alkaline reserve simultaneously. The main effect is due to the Nanoparticles which can consolidate and act as alkaline source to recover the paper mechanical properties and limit further degradation. At the same time the TBAB/HPMC improves the effectiveness of the formulation adding a reductive action on the carbonyl groups. The role of the HMPC as consolidator is not predominant at the tested concentration (0.1 %w/w), and data at higher concentration of the polymer will be investigated to improve formulation performance.

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