




# Polyvinyl alcohol and allyl $\alpha$ , $\alpha'$ -trehalose copolymers for a sustainable strengthening of degraded paper

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## Abstract

Acid-catalyzed hydrolysis of glycosidic bonds is the most important degradation mechanism affecting cellulose-based materials. It results in the decrease of DP and in the loss of the original mechanical properties. The neutralization of acidity is therefore one of the most efficient ways to hamper the degradation of cellulosic artworks. However, in the case of acidic and strongly degraded artifacts, in addition to deacidification, a consolidation treatment must be performed. To this aim, a new class of biopolymers, obtained by a synthetic procedure that considers the principles of Sustainable Chemistry, was investigated. Three allyl saccharide/vinyl acetate copolymers, having different molar ratios between starting monomers, were prepared using  $\alpha$ , $\alpha'$ -trehalose, and used to synthesize the corresponding allyl saccharide/vinyl alcohol copolymers. The use of saccharide derivatives as monomers improves the affinity and compatibility of the biopolymer with the artifacts to be treated. After characterization, the efficacy of the copolymers in the strengthening of degraded paper was evaluated with mechanical tests. The most effective system was thus selected for further testing. Its performance was compared to that of Klucel G<sup>®</sup>, a commercial product belonging to the class of cellulose derivatives, which are largely used in conservation practice.

## KEYWORDS

applications, biopolymers, cellulose, other wood products, renewable polymers

## 1 | INTRODUCTION

Cellulose is a linear polymer of D-glucose that plays a fundamental role in the mechanical properties of paper. The degree of polymerization (DP) of native cellulose ranges between 9000 and 15,000,<sup>1</sup> and it is usually reduced during the paper manufacturing processing and after natural aging of paper documents.

Several scientists and conservators have been recently brought attention to the increasing number of cellulosic

artifacts needing urgent intervention.<sup>2–6</sup> Effective and innovative conservation strategies should be developed with the aim of transferring these objects, which constitute a large part of the global patrimony of mankind, to future generation.

The most important degradation mechanism affecting cellulose-based materials is the acid-catalyzed hydrolysis of  $\beta$ -1,4-glycosidic bonds, which results in the decrease of DP and, macroscopically, in the loss of the original mechanical properties.<sup>7–9</sup> For this reason, the neutralization of acidity

in materials, commonly indicated with the term “deacidification,” is a potential way to hamper the degradation of these works of art. To that aim, calcium or magnesium hydroxide nanoparticles dispersed in short-chain alcohols, also known as alkaline nanoparticles, have been successfully used on paper and canvas<sup>10–17</sup> and on wood.<sup>18–21</sup>

Due to the fact that cellulose-based artifacts lose their original mechanical properties upon natural aging, a reinforcement is usually needed. Different approaches can be used to this purpose. If the original cellulose constituting textile fibers of paint canvas or paper manuscripts incurred in a pronounced depolymerization, conservators may proceed with a relining for canvases<sup>22</sup> or with a mending using Japanese paper and adhesives for paper.<sup>23</sup> Such interventions are definitely invasive and, when possible, alternative methods have to be considered, such as the creation of a consolidating coating layer at molecular level, with less visual impact of the treatment.<sup>24</sup> In that sense, acrylics and other industrial polymers can be potentially used to that aim, but they are not chemically compatible with cellulose and may present several drawbacks upon natural aging.<sup>25,26</sup> Therefore, more compatible formulations have been recently envisaged. Saccharides,<sup>27,28</sup> natural polysaccharides or their derivatives,<sup>29,30</sup> and oligomers based on natural molecules with polar structure similar to the linear form of saccharides<sup>31,32</sup> have been studied for the treatment of cellulosic materials as wood, paper or fabrics, providing materials with chemical, physical and mechanical properties similar to those of cellulose.

However, the most challenging issue is to develop compatible formulations that are also respectful of substrates, such as historical documents and precious drawings, which are usually highly sensitive to water because of the presence of inks, pigments and dyes. In other terms, the consolidating agent must be indeed compatible with cellulose, but also soluble in solvents or blend of solvents with lower polarity than neat water. The solubility of the above-mentioned biopolymers, that are potentially effective for consolidation, in solvents or solvents mixtures usually safe to the objects, is very limited, so that their use for conservation purposes is hindered.

With the aim of obtaining polymers that are compatible with cellulose and soluble in solvents or solvents mixtures less polar than water, therefore targeted to a safe intervention on fragile paper artifacts, we modified a class of recently developed systems,<sup>33</sup> already tested as archeological wood consolidant.<sup>34</sup>

The biopolymers were synthesized starting from vinyl acetate (VAc) and allyl  $\alpha,\alpha'$ -trehalose, so to obtain, through hydrolyzation, the corresponding allyl saccharide/vinyl alcohol copolymers. The rationale behind this

copolymerization is the following: Polyvinyl alcohol is a really good candidate as a strengthening agent, and it is widely used as an adhesive for paper, but it is only soluble in water and its compatibility with paper is limited.  $\alpha,\alpha'$ -trehalose is a nonreducing disaccharide with a symmetrical structure, which has high stability against acids and heat<sup>35,36</sup> and can be used for the synthesis of biomonomers, such as allyl  $\alpha,\alpha'$ -trehalose. Carbohydrates are of great interest being inexpensive and readily available and can be incorporated in the main chain of several polymers<sup>37</sup> or added as pendant groups.<sup>38</sup> Here, the presence of  $\alpha,\alpha'$ -trehalose is expected to increase the solubility of the copolymers in solvents or solvents mixtures less polar than water, and to act as an active moiety to stably interact with cellulose.

Using  $\alpha,\alpha'$ -trehalose as renewable feedstock, three allyl  $\alpha,\alpha'$ -trehalose/vinyl alcohol copolymers, with different molar ratios between monomers, were prepared to find the best composition for paper treatment. The efficacy of the three copolymers in the strengthening of degraded paper was evaluated with preliminary tensile tests. The most effective system was thus selected for further testing, including the application on naturally aged paper (NAP), whose original mechanical properties are completely lost. The performance of the new biopolymer was compared to that of Klucel G<sup>®</sup>, a commercial product selected as a reference material belonging to the class of cellulose derivatives, which are largely used in conservation practice. A two-step treatment, aimed at the neutralization of acidity using alkaline nanoparticles and at the strengthening of cellulose using the selected allyl saccharide/vinyl alcohol copolymer, was also investigated.

## 2 | MATERIALS AND METHODS

### 2.1 | Materials

Metal granular calcium (99%),  $\alpha,\alpha'$ -trehalose dehydrate (99%), allyl bromide (99%), hydrochloric acid (37%), ethanol (99.5%), methanol (99.8%), isopropanol (> 99.5%), VAc (>99.0%), potassium bromide (>99%), D<sub>2</sub>O (99.8%), and CD<sub>3</sub>OD (99.8%) were purchased from Sigma Aldrich (Germany). Potassium hydroxide (>85%) and sulfuric acid (96%), were purchased from Carlo Erba (Italy). 2,2'-Azobisisobutyronitrile (AIBN) was purchased from Fluka Co. Acetone (>99%) was purchased from VWR International. All the chemicals were reagent grade and were used without further purification. Klucel G<sup>®</sup> (hydroxypropylcellulose, technical grade) was purchased from Phase Restauro (Italy). Highly pure water (having a resistivity of 18 M $\Omega$  cm) was produced by a Millipore Milli-Q UV system.

## 2.2 | Strengthening agents' synthesis

Allyl  $\alpha,\alpha'$ -trehalose/vinyl alcohol (AT/VA) copolymers were synthesized starting from a procedure described in the literature<sup>33</sup> modifying the molar ratios between the starting monomers. AT was synthesized from allyl bromide and  $\alpha,\alpha'$ -trehalose with molar ratio 4:1, obtaining a product with a Degree of Substitution ( $DS_{AT}$ ) of 1.3. The allyl saccharide was then used to prepare three allyl  $\alpha,\alpha'$ -trehalose/VAc (AT/VAc) copolymers, having different molar ratios between the starting monomers, which are labeled as C1, C2, and C3 (see Table 1). The hydrolysis of AT/VAc copolymers resulted in the corresponding AT/VA copolymers, which are labeled as C1H, C2H, and C3H. Detailed information about preparation and characterization of the two classes of biopolymers are indicated in the following paragraphs.

### 2.2.1 | Synthesis of AT/VAc copolymers

VAc and allyl  $\alpha,\alpha'$ -trehalose in methanol (2.5 mL) were added in a Sovirel<sup>®</sup> tube under nitrogen atmosphere; AIBN (17.45 mg) was then added and the reaction mixture was allowed to react at 90°C for 6 h under continuous stirring. After cooling to room temperature, the solvent and the residual VAc were distilled at reduced pressure. The solid residue was extracted in acetone and the soluble fraction was distilled at reduced pressure obtaining a pale orange solid (for C2:  $M_n = 4800 \text{ g mol}^{-1}$ ;  $M_w = 64,200 \text{ g mol}^{-1}$ ),<sup>33</sup> which was characterized by <sup>1</sup>H-NMR ( $CD_3OD/400 \text{ MHz}$ ) and FT-IR (KBr pellets) spectroscopies. <sup>1</sup>H-NMR ( $CD_3OD$ , 400 MHz, ppm): 1.84 (m, 2H,  $CH_3-COO-CH-CH_2-$  VAc unit); 2.00, 2.03, 2.05 (m, 3H,  $CH_3-COO-CH-CH_2-$  VAc unit); from 3.40 to 4.50 (m, 12H,  $H_2-H_6$ ,  $H_2'-H_6'$  and 2H,  $-CH_2-CH=CH_2$  allyl group); 4.87 (m, 1H,  $CH_3-COO-CH-CH_2-$  VAc unit); from 5.05 to 5.38 (m, 2H,  $H_1$ ,  $H_1'$  and 2H,  $-CH_2-CH=CH_2$  allyl group); 5.95 (m, 1H,

$-CH_2-CH=CH_2$  allyl group). FT-IR (KBr pellets): peaks at 3435 (s, O—H stretching); 2935 (m, C—H stretching); 1736 (s, C=O stretching acetate group); 1647 (m, C=C stretching); 1433, 1375 (m,  $CH_3-$  bending acetate group); 1244 (s, C—O stretching acetate group); 1146, 1105, 1080, 1043, 1024, 995 (s, C—OH stretching, C—O—C stretching); 945 (m, =C—H out of plane bending)  $cm^{-1}$ .

### 2.2.2 | Synthesis of AT/VA copolymers

A solution of the allyl  $\alpha,\alpha'$ -trehalose/VAc copolymer in anhydrous methanol (19%) was added under nitrogen atmosphere to a solution of KOH in anhydrous methanol (1%) (volume ratio 1.4:1) using a dropping funnel. After 1 h at 50°C under continuous stirring, the final mixture was dried under vacuum at room temperature and the solid residue was characterized by <sup>1</sup>H-NMR ( $D_2O/400 \text{ MHz}$ ) and FT-IR (KBr pellets) spectroscopies. <sup>1</sup>H-NMR ( $D_2O$ , 400 MHz, ppm): 1.61, 1.64, 1.68, 1.70 (m, 2H,  $CH_2-CH[OH]-$  vinyl alcohol unit); from 3.39 to 4.20 (m, 12H,  $H_2-H_6$ ,  $H_2'-H_6'$ , 1H,  $CH_2-CH[OH]-$  vinyl alcohol unit and 2H,  $-CH_2-CH=CH_2$  allyl group); 5.18 (m, 2H,  $H_1$ ,  $H_1'$ ); from 5.24 to 5.39 (m, 2H,  $-CH_2-CH=CH_2$  allyl group); 5.96 (m, 1H,  $-CH_2-CH=CH_2$  allyl group). FT-IR (KBr pellets): peaks at 3355 (s, O—H stretching); 2937 (m, C—H stretching); 1747 (w, C=O stretching acetate group); 1645 (m, C=C stretching); 1436 (m,  $CH_3-$  bending acetate group); 1144, 1104, 1082, 1051, 993 (s, C—OH stretching, C—O—C stretching); 942 (w, =C—H out of plane bending)  $cm^{-1}$ .

<sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectra were recorded with a Varian Mercury Plus 400 spectrometer and a Varian VXR 200 spectrometer working at 399.921 MHz and 199.985 MHz, respectively. The chemical shifts are reported in ppm and referred to tetramethylsilane (TMS) as internal standard. Spectra elaboration was performed with the software MestRe-C 4.3.2.0.

The VAc/AT ratio for each final copolymer was evaluated by the ratio between the integrals of the NMR signals characteristic of the two monomeric units

**TABLE 1** Composition of  $\alpha,\alpha'$ -trehalose/vinyl acetate (AT/VAc) copolymers with different monomers molar ratio

	C1	C2	C3
VAc (mg)	393	430	454
VAc (mmol)	4.6	5.0	5.3
AT (mg)	272	150	63
AT (mmol)	0.69	0.38	0.16
VAc/(AT $\times$ DS <sub>AT</sub> ) <sup>a</sup>	5	10	25
Acetone soluble fraction (mg)	328	109	370
Acetone soluble fraction yield (%)	48	65	70

<sup>a</sup>DS<sub>AT</sub> = 1.3.

considering for each signal the number of hydrogen atoms that generated it and taking into account the overlapping of different signals, as follows:

$$\text{ratio between the copolymer units} = \frac{X_{\text{VAc}}}{X_{\text{AT}}}$$

where

$$X_{\text{VAc}} = \frac{\text{Integral signal at 1.84 ppm}}{2}$$

and

$$X_{\text{AT}} = \frac{\text{Integral signal (3.40 ppm} - 4.20 \text{ ppm)}}{12 + (2 \cdot \text{DS})}$$

Similarly, the VA/AT ratio for each hydrolyzed copolymer was calculated as the ratio between the signal intensities due to the vinyl alcohol units and those due to the saccharide units corrected for the overlapping with the VA signal, as follows:

$$\text{ratio between the copolymer units} = \frac{X_{\text{VA}}}{X_{\text{AT}}}$$

where

$$X_{\text{VA}} = \frac{\text{Integral signal (1.61} - 1.70 \text{ ppm)}}{2}$$

and

$$X_{\text{AT}} = \frac{\text{Integral signal (3.39 ppm} - 4.20 \text{ ppm)} - X_{\text{VA}}}{12 + (2 \cdot \text{DS})}$$

FT-IR spectra were recorded with a Shimadzu IRAffinity-1S model and elaborated with the software Shimadzu IRsolution v. 2.16. Spectra of solid samples were recorded using KBr pellets.

## 2.3 | Nanoparticles synthesis

Calcium hydroxide nanoparticles were prepared using a solvothermal synthesis, starting from ethanol and calcium metal. More in detail, 10 g of granular calcium and 500 mL of ethanol were placed inside a high-pressure reactor (Parr-instruments). Before starting the reaction, vacuum/nitrogen cycles were performed to ensure an oxygen-free atmosphere inside the sealed reaction chamber. During the first step of the reaction, calcium alkoxide is obtained. To hydrolyze the alkoxide to calcium

hydroxide, 35 mL of water was added inside the reaction chamber by means of steel pipette in a nitrogen atmosphere. The addition was carried out at 70°C and the system was stirred for 60 min. Synthesized calcium hydroxide nanoparticles are hexagonal platelets with a high degree of ordering, having a thickness of about 20–30 nm and an average diameter of about 150–200 nm.<sup>20,39</sup>

## 2.4 | Aging of filter paper

Filter paper (qualitative filter papers composed of cellulose fiber and manufactured from high-quality cotton linters treated to maximize alpha cellulose, paper grammage: 75 g m<sup>-2</sup>, particle retention 4 μm) was used to test the efficacy of several selected systems. Paper sheets were immersed in a sulfuric acid solution (pH = 2.5, 3.2 mM) for 30 s and then aged at high temperature and relative humidity (80°C and 75% RH) for 10 days. These samples are labeled as AP, that is, aged paper. Unaged filter paper was characterized and used as a reference system. This system is labeled as P.

## 2.5 | Preliminary tests on aged paper using AT/VA copolymers

The three copolymers were dispersed in an isopropanol/water mixture (50% vol) at a concentration of 18.5 g L<sup>-1</sup> and 5 mL of each dispersion was applied on aged filter paper samples (9 × 8 cm<sup>2</sup>) by means of a brush. After the treatment, samples were left to dry at room temperature for at least 2 days. The weight increase due to treatment ranged from about 10%–15%. Name and composition of paper samples are indicated in Table 2.

Prior to testing, samples were equilibrated for at least 24 h at 23°C and 50% RH. For these preliminary tests, tensile strength measurements were conducted on small paper strips (1 × 8 cm<sup>2</sup>) using a TA Instrument Hybrid Rheometer DISCOVERY HR-3, equipped with a Film Tension Dynamic Mechanical Analysis tool. The used procedure was adapted from standards of tensile measurements on paper,<sup>40,41</sup> and it provides reliable preliminary indications even using small amounts of samples such as those available during the earliest steps of a new material development. During measurements, the paper strip was clamped on two jaws, whose distance was fixed at 4 cm. The rate of separation of the two jaws was set at 94 μm s<sup>-1</sup>. This rate of grip separation generally results in sample rupture in 10–30 s. Nine measurements were performed for each series of samples. The mean value of the maximum force at break was therefore calculated.

**TABLE 2** Name and composition of the treated paper samples (SA: Strengthening agent, NanoP: Alkaline nanoparticles for deacidification)

Preliminary tests		
Name	SA type	NanoP type
C1H	AT/VA copolymer	—
C2H	AT/VA copolymer	—
C3H	AT/VA copolymer	—
Final application		
Name	SA type	NanoP type
KG	Klucel G <sup>®</sup>	—
C2H	AT/VA copolymer	—
OH	—	Ca(OH) <sub>2</sub>
C2H + OH	AT/VA copolymer	Ca(OH) <sub>2</sub>

## 2.6 | Application of selected systems on aged paper

After preliminary tests, the AT/VA copolymer showing the most interesting features, that is, C2H, was selected for additional tests. The strengthening agent was dispersed in isopropanol at a concentration of 5 g L<sup>-1</sup> to be used on paper disks (diameter = 55 mm) or 6 g L<sup>-1</sup> to be used for paper strips (1.5 × 15 cm<sup>2</sup>). 5 mL was sprayed on each paper sample (about 1.05 g/cm<sup>2</sup> for paper disks and about 1.18 g/cm<sup>2</sup> for paper strips).

A second series of paper samples was treated with Klucel G<sup>®</sup>, a commercial cellulose derivative used in conservation practice, which is to be considered a state-of-the-art method. The product was applied with the same methodology described above, using the same concentrations in isopropanol. These samples are labeled as KG.

To evaluate the effect of deacidification on the mechanical properties of paper, about 1.5 mL of calcium hydroxide nanoparticles in ethanol (3 g L<sup>-1</sup>) were applied on another set of samples, which are labeled as OH.

A fourth series of samples, labeled as C2H + OH, was treated with calcium hydroxide nanoparticles and the AT/VA copolymer. More in detail, samples were firstly treated with calcium hydroxide nanoparticles and left at 50% RH for 14 days, time needed for calcium hydroxide excess to turn into carbonate. Then, the copolymer was applied on deacidified paper samples. Both treatments were applied following the applicative procedures indicated above.

It is worth noting that, for these additional tests, an applicative procedure more respectful of the artworks was chosen, that is, an approach based on waterless systems applied at a lower concentration by spraying, which,

differently from the brush, does not imply a contact with the surface to be treated.

### 2.6.1 | Tensile strength measurements

Tensile strength measurements were conducted on paper strips using a Hounsfield H10 KS universal testing machine. These measurements were performed following an international standard for the determination of tensile properties at a constant rate of elongation (20 mm/min).<sup>42</sup> Before testing, the samples were equilibrated at 20°C and 65% relative humidity by keeping them in a climate-controlled room for at least 24 h. Each paper strip measured 1.5 × 15 cm<sup>2</sup> and was clamped on two jaws. Ten measurements in machine direction were performed for each series of samples. The mean value of the load at which sample rupture occurred was used to calculate the Ultimate Tensile Strength (UTS), given by:

$$UTS = AF/W \text{ [kN/m]}$$

where AF is the axial force at rupture and W is the width of the sample. Elongation at rupture (E) was also calculated for each series of samples.

### 2.6.2 | Bursting strength measurements

Bursting strength (BS) measurements were conducted on filter paper disks using a Messmer Buchel M425000 testing machine. These measurements were performed following an international standard.<sup>43</sup> Each filter paper disk (diameter = 55 mm), held between annular clamps, was subjected to an increasing pressure by a rubber diaphragm, which was expanded by hydraulic pressure at a controlled rate. The pressure value at the instant of rupture is the BS.

### 2.6.3 | pH measurements

For pH measurements of paper, 125 mg of sample was weighed, cut in small pieces and placed inside screw top vials. The 9 mL of distilled water was added inside each vial, subsequently sealed to avoid the solubilization of CO<sub>2</sub> from air into the extracting water. Vials were kept under stirring for 1 h, before measuring the pH of the extraction by using a digital pH-meter (CrisonBasic 20, equipped with a combined electrode, model 52–21). Three measurements were performed on each sample. The error associated to pH measurements on these samples is ±0.2.



## 2.6.4 | DP measurements

Viscosimetric determinations of the DP<sub>v</sub> were performed only on filter paper before and after the artificially aging.<sup>44</sup> The data are presented in terms of scissions per initial cellulose chain (S\*), calculated using the following equation<sup>45,46</sup>:

$$S^* = DP_{V_0}/DP_{V_t} - 1$$

where DP<sub>V<sub>0</sub></sub> is the DP at time zero, and DP<sub>V<sub>t</sub></sub> is the DP at time t. It is worth noting that an accurate calculation of the number of scission cannot be extracted from DP<sub>v</sub>, due to the fact that polydispersity cannot be assessed by viscosimetric determinations.<sup>47</sup> Nevertheless, in the present work, the comparison of S\* values calculated from DP<sub>v</sub> can be considered fully acceptable, because the experimental data refer to homologous series of samples. The error associated to these measurements is ±25.

## 2.6.5 | Morphological characterization

The morphology of filter paper samples was investigated by means of field emission scanning electron microscopy (FE-SEM), using a Zeiss SIGMA FE-SEM (Carl Zeiss Microscopy GmbH, Jena, Germany). Paper samples were placed over aluminum stubs using a conductive tape and coated with a thin layer of gold (about 15 Å) with a sputter coater. Image were acquired using an accelerating voltage of 25 kV and a working distance of about 8 mm. Energy dispersive X-rays spectroscopy (EDX) was carried out using a X-act Silicon Drift Detector (Oxford Instruments, England).

## 2.7 | Application on NAP

The same treatments indicated in Section 2.6 were tested on a paper sheet from the beginning of 19th century. The paper was produced starting from rags, and, due to the low pH (about 4), it has a low DP (about 300, obtained by viscosimetric measurements), and, consequently, is very fragile.

From a single paper sheet, five samples were obtained (10 × 1.5 cm<sup>2</sup>). These samples are labeled as NAP, that is, NAP. Samples were treated using the same procedure reported in Section 2.2. Due to the fragility of the samples, and to the small amount of material available, tensile strength measurements were not performed. Nevertheless, the mechanical resistance of treated and untreated samples was evaluated performing some folding tests based on the following procedure: the specimens

were manually subjected to a first bending test, to evaluate the improvement in paper elasticity. Each specimen was bent 10 consecutive times and held in the maximum flexion position for 10 s evaluating the ease of breaking. With the same procedure, the mechanical resistance was also evaluated on samples of reduced length (5 × 1.5 cm<sup>2</sup>).

The morphology of NAP samples was investigated by means of FE-SEM, using the same procedure of filter paper samples. EDX mapping of calcium was performed with a X-act Silicon Drift Detector (Oxford Instruments, England).

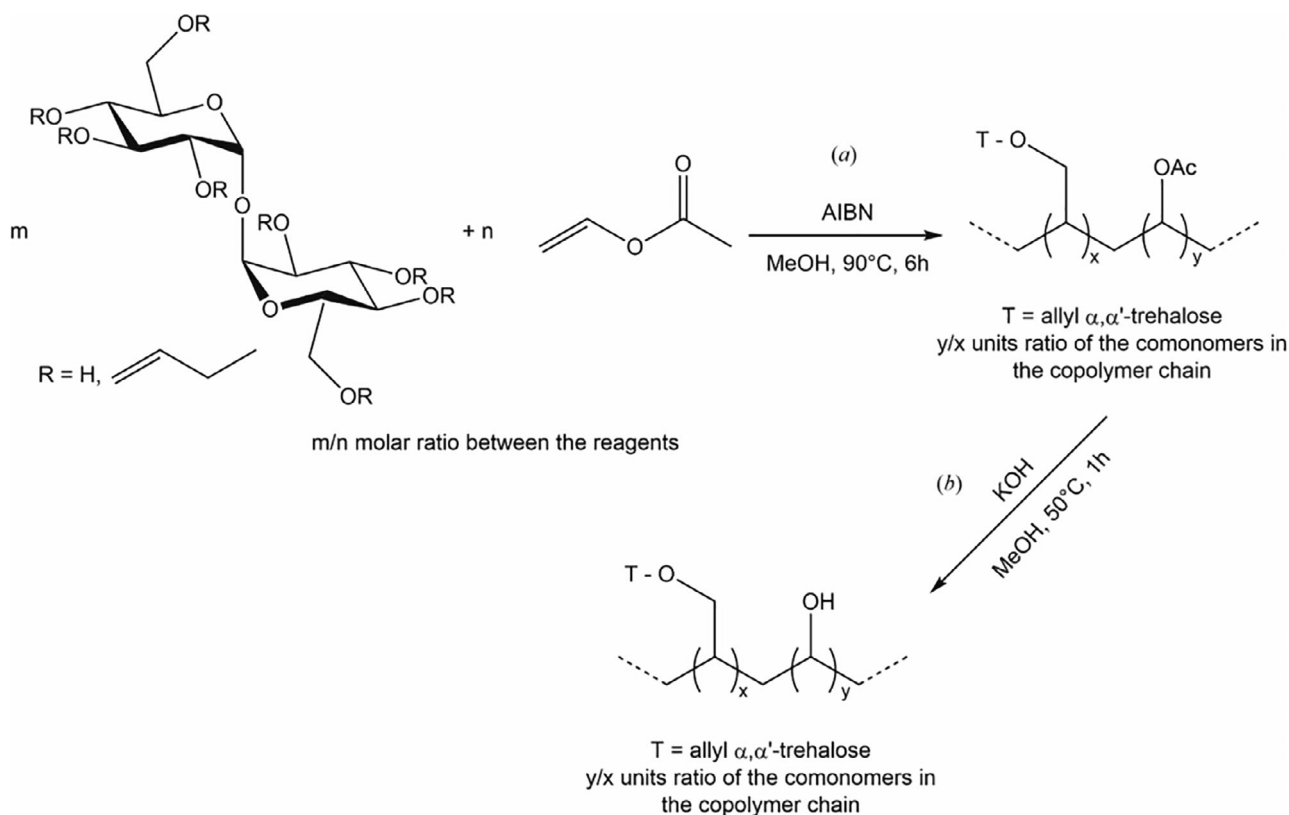
Colorimetric measurements were carried out by using a portable spectrophotometer X-Rite SP60. For each sample, three measurements were performed on each spot previously selected and located by using a mask. Results were elaborated and reported in CIE-L\*a\*b\* standard color system: for each defined spot on a sample the average value of L\*a\*b\* was used, where L\* indicates the brightness and ranges from 0 (black) to 100 (white); a\* and b\* are the color axes and their values range from -60 to +60. On the a\* axis, positive values indicate amount of red, whereas the negative ones indicate green. On the b\* axis, yellow is positive while blue is negative. The color difference between samples was expressed in terms of the ΔE\* parameter, calculated from the colorimetric coordinates and L\*, a\*, and b\*, following the CIEDE2000 definition.<sup>48</sup> A ΔE\* of 3 is commonly regarded as the detection limit of human eyes.<sup>49</sup> Measurements were performed before and after the aging of filter paper and after application of the polymer on paper samples.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Synthesis and characterization of AT/VA copolymers

The biopolymers used in this study were prepared starting from α,α'-trehalose, according to a procedure reported in the literature.<sup>33</sup> The α,α'-trehalose is widely found in bacteria, fungi, plants and invertebrates and has high stability against acids and heat.<sup>35,36</sup> Being a non-reducing disaccharide, it consequently allows for a direct functionalization of the molecule and it is, therefore, widely used for the synthesis of biomonomers.

The reaction scheme of the preparation of allyl α,α'-trehalose/vinyl alcohol (AT/VA) copolymers is reported in Scheme 1. This synthetic methodology allowed us to produce consolidants that have structure similar to that of the cellulosic substrate using monomers obtained from renewable sources. The use of building blocks obtained from renewable raw materials is also in accordance with the principles of Sustainable Chemistry.



**SCHEME 1** Synthesis of the vinyl acetate copolymers (a) and of the vinyl alcohol copolymers (b)

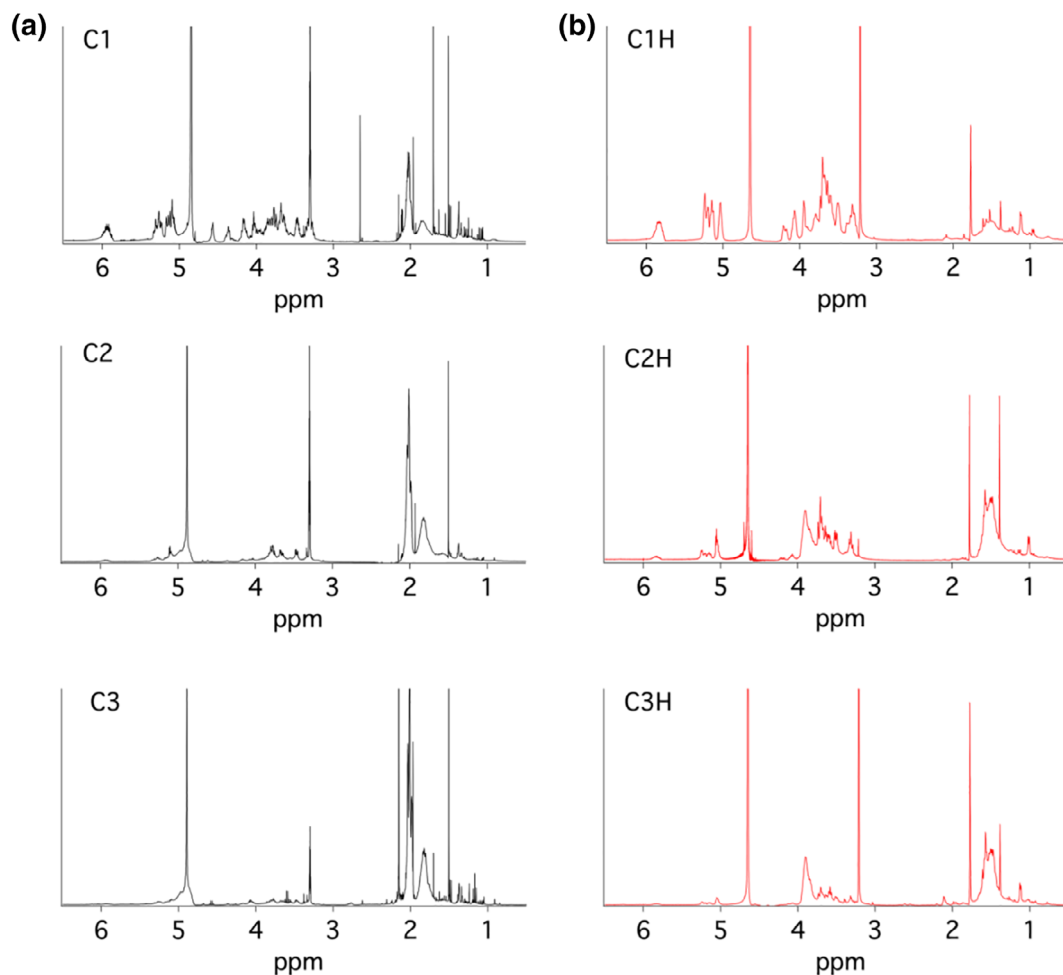
Allyl  $\alpha, \alpha'$ -trehalose was synthesized from allyl bromide and  $\alpha, \alpha'$ -trehalose<sup>32</sup> obtaining a product with a DS of 1.3.<sup>33</sup> The DS and purity for the allyl  $\alpha, \alpha'$ -trehalose were checked via <sup>1</sup>H-NMR. The introduction of the allyl group into the saccharide structure allows to obtain biocopolymers with saccharide units by means of a radical copolymerization with vinyl monomers. In fact, the allyl saccharide was used for the synthesis of VAc copolymers with different molar ratios between the monomers (see Table 1). The mechanism for copolymerization reaction is a standard free radical polymerization; at the end of the reaction, free radicals do not remain in the solution.

Due to the lower reactivity of the allyl group with respect to the vinyl one, the presence of AT is expected to partially hamper the polymerization reaction. In fact, it has been previously demonstrated that the presence of significant amount of allyl groups reduces the molecular weight of the final AT/VAc copolymers.<sup>33</sup> Furthermore, the use of AT monomers mono- or disubstituted, such as those synthesized for the present study ( $DS_{AT} = 1.3$ ), reduces the possibility of cross-linking during the polymerization and favors the formation of linear chains. Both these features are expected to hamper the increase of the molecular weight, thus favoring the penetration of the strengthening agents inside the material to be treated during the application.

At the end, the AT/VAc copolymers were hydrolyzed to the corresponding vinyl alcohol copolymers. The rationale behind the hydrolysis of AT/VAc copolymers to AT/VA is twofold: firstly, the presence of polar groups favors the interaction of the strengthening agents with the hydroxyl groups of cellulosic substrates; second, the hydrolysis of acetate groups can prevent the release of acetic acid that may take place after the application upon the natural aging of the treated objects, which, in turn, can trigger the depolymerization of cellulose.

All AT/VAc and AT/VA copolymers were characterized by NMR and FT-IR spectroscopy (see Figure 1 and Figure 2). Signals of comonomers are found in all the spectra of the two series of biopolymers, even if, as expected, those signals display different relative intensities, depending on the different starting ratios between monomers.

In particular, the comparison of the integral of the signals due to each comonomer, as obtained by the <sup>1</sup>H-NMR spectra, was used to evaluate the ratio between the monomer units in the synthesized products. More specifically, the VAc/AT ratio for each copolymer was evaluated by the ratio between the integrals of the NMR signals characteristic of the two monomeric units considering for each signal the number of hydrogen atoms that generated it and taking into account the overlapping of different



**FIGURE 1** (a)  $^1\text{H}$ -NMR spectra of AT/VAc copolymers. (b)  $^1\text{H}$ -NMR spectra of AT/VA copolymers [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

signals. Similarly, the VA/AT ratio for each hydrolyzed copolymer was calculated as the ratio between the signal intensities due to the vinyl alcohol units and those due to the saccharide units corrected for the overlapping with the VA signal (see Section 2.2 for further detail).

The ratio between the monomeric units evaluated by NMR spectroscopy is reported in Table 3. As expected, the intensity of the VAc and vinyl alcohol signals is higher in the spectra of C3 and C3H copolymers than in C2 and C2H and C1 and C1H copolymers while for C1 and C1H copolymers the presence of chains richer in saccharide units was observed. It is also worth noting that the experimental VAc/AT ratio in samples C2 and C3 is similar to the starting values reported in Table 1, while a higher difference is found for the system featuring a higher content of AT, that is, C1. In general, the presence of AT is expected to partially hamper the polymerization reaction, as it produces stable radicals with low reactivity that eventually result in a decrease of the conversion of VAc, which is proportional to the concentration of

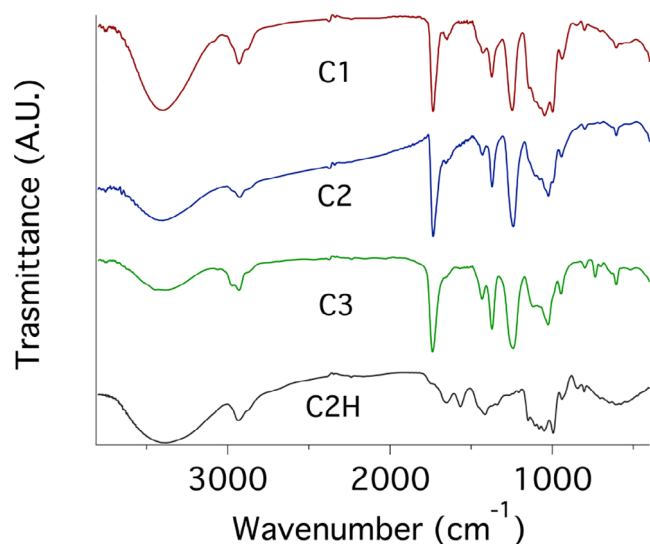
AT. Based on the data reported in Table 3, this hindering effect seems to be critical when the amount of AT is significant, such as in sample C1, where the starting VAc/ATR ratio is 5 and the final value is about 60% lower than expected. Finally, it is worth noting that the VA/AT values are not significantly affected by the hydrolysis, being very similar to the corresponding VAc/AT values.

The FT-IR spectra of the three AT/VAc copolymers, reported in Figure 2, confirm what shown in the  $^1\text{H}$ -NMR spectra, highlighting the presence of different quantities of the two comonomers, as indicated by the relative intensity of the bands due to the ester group of the vinyl units ( $1740\text{ cm}^{-1}$ ) and the bands due to the saccharide units (between  $1000$  and  $1050\text{ cm}^{-1}$ ). As a result of the hydrolysis of the AT/VAc, the signal of the ester group at about  $1740\text{ cm}^{-1}$  is significantly reduced, as shown, for instance, in the C2H sample spectrum reported in Figure 2, in agreement with a high degree of conversion.

It is important to note that, due to the weak intensity of the residual signals of the non-hydrolyzed VAc units



and the overlapping of the vinyl alcohol units signal (4.00 ppm, CH<sub>2</sub>-CH(OH)-) with that of the saccharide structures, it was not possible to assess the degree of hydrolysis using the general procedure based on the integral values of the <sup>1</sup>H-NMR signals of VAc (2.00 ppm, CH<sub>3</sub>-CO) and vinyl alcohol (4.00 ppm). However, in general, the signals of the VAc units in FTIR and <sup>1</sup>H-NMR spectra of hydrolyzed biopolymers have very low intensities; this fact allowed us concluding that the hydrolysis was almost complete. It is worth recalling that the hydrolyzed biopolymers are expected to better interact with cellulosic substrates, due to the presence of -OH moieties, and not to release acetic acid during the natural aging, which could in turn promote the acid-catalyzed hydrolysis of glycosidic bonds of cellulose.



**FIGURE 2** FT-IR spectra of AT/VAc copolymers, namely C1 (red), C2 (blue), C3 (green). The spectrum of AT/VAc copolymer, namely C2H (gray) is also reported, as representative of the hydrolyzed copolymers [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

**TABLE 3** Ratio between the monomer units in the AT/VAc and AT/VA copolymers, as obtained by <sup>1</sup>H-NMR spectra

Sample name	VAc/AT	Sample name	VA/AT
C1	1.8	C1H	2.2
C2	8.5	C2H	9.9
C3	23.5	C3H	20.1

**TABLE 4** Properties of filter paper (P) and aged filter paper (AP)

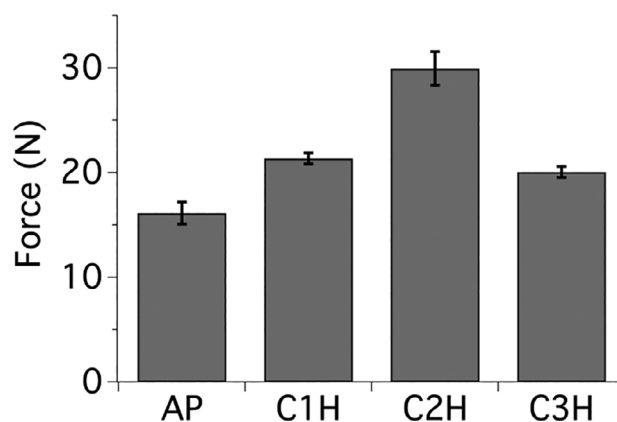
Sample name	pH	UTS (kN m <sup>-1</sup> )	E (%)	BS (kPa)	S*
P	7.0	2.85 ± 0.11	1.67 ± 0.10	97.1 ± 3.5	—
AP	4.5	2.35 ± 0.10	1.89 ± 0.15	90.0 ± 3.8	0.18

### 3.2 | Preliminary tensile tests using AT/VA copolymers

Filter paper was used to test the efficacy of all the synthesized copolymers in the reinforcement of degraded materials. To that aim, as indicated in Section 2.4, filter paper was acidified with sulfuric acid solution (pH 2.5) and then aged at high temperature and relative humidity for 10 days. The paper, whose pH after the acidification was 4.5, at the end of the aging displayed a decrease in DP of about 0.18, expressed in terms of S\*, that is, scissions per initial cellulose chain (see Table 4). As a result of the aging procedure, a ΔE\* of 3.8 was measured.

For these preliminary tests, an isopropanol/water mixture (50% vol) was used to disperse the copolymers. It must be noted that the use of treatments dispersed or solubilized in neat water on paper samples are discouraged. In fact, water promotes the swelling of cellulose fibers, resulting in a decrease of the mechanical properties.<sup>50,51</sup> In addition to that, neat water may cause the solubilization of original compounds from paper objects, that is, sizing agents and inks.

In Figure 3, the maximum force at break of paper samples, before and after the treatment, is reported. It is worth noting that a significant increase in the mechanical properties is shown by all the treated samples. More specifically, an increase of about 25% (20 N vs. 16 N) is displayed by C3H, which was treated with the copolymer featuring the highest amount of vinyl alcohol units. The



**FIGURE 3** Maximum force at break of aged filter paper before and after treatment with the three AT/VA copolymers, measured with a film tension DMA tool (see Section 2.5)

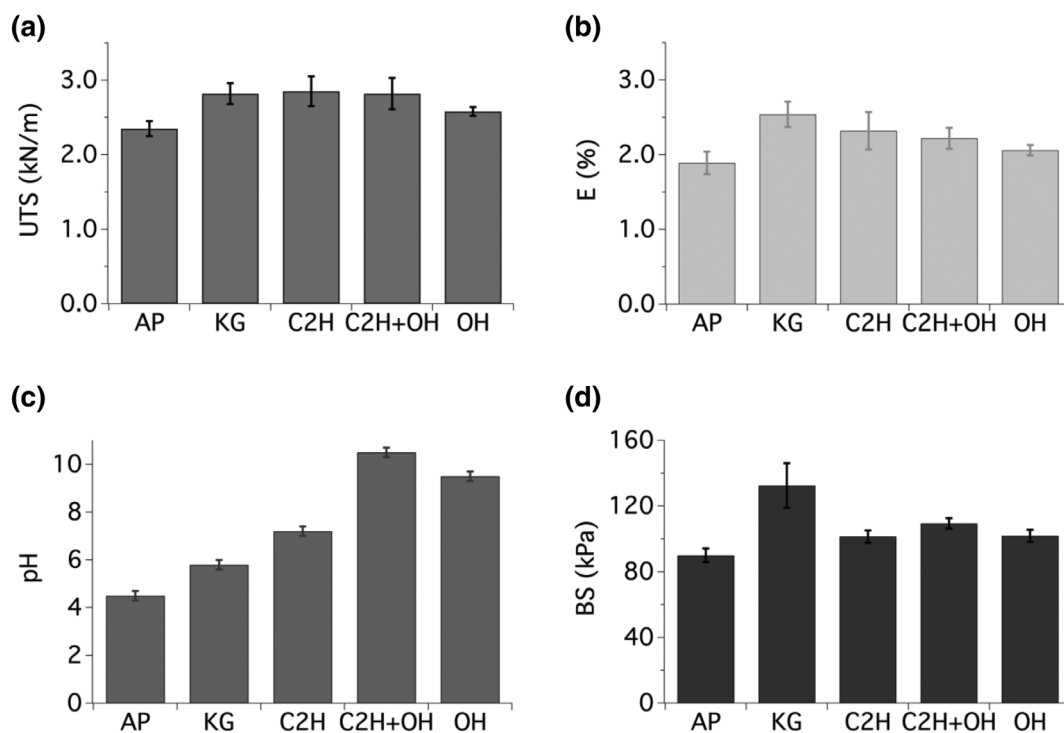
weight increase of samples after the application of C3H is about 10%, while specimens treated with C1H and C2H show a weight increase of about 15%. This difference is probably due to the lowest solubility of the C3H in the isopropanol/water mixture chosen for the application and might explain the different consolidating effect shown in Figure 3. In fact, higher amounts of VAc units are expected to favor the copolymerization but, at the same time, once hydrolyzed to vinyl alcohol, the higher interactions between hydroxyl groups of different copolymer chains may reduce the solubility of the final product in polar solvents, such as the mixture selected for the tests. The slightly worst performance of C3H with respect to the other synthesized systems can be probably also ascribed to the low amount of AT units in the chain, which may not allow for an effective bonding to the cellulosic network.

An increase of about 30% (21 N vs. 16 N) in the maximum force at break is shown by C1H, which was obtained starting with the lowest VAc/AT ratio. As previously indicated, the weight increase of samples C1H and C2H is similar, even if a different consolidating effect is obtained (see Figure 3). This is probably due to the low molecular weight of the copolymer C1H, which probably hampers the strengthening effect. In fact, as previously observed,<sup>33</sup> the presence of higher amount of AT in the

chain reduces the molecular weight due to the lower reactivity of the allyl group with respect to vinyl monomers, even if it allows to obtain a final product that is more soluble in water or alcohols and has a higher amount of saccharides units. Overall, the best results were obtained with the C2H system that granted an increase in the maximum force at break of about 100% with respect to aged paper (30 N vs. 16 N), showing that a final VA/AT ratio of ten provides good consolidating effects and, at the same time, grants the solubilization of the biopolymer in solvents that are less polar than water, including isopropanol, allowing for a treatment that is more respectful of the original materials. On the basis of these preliminary results, the copolymer C2H was selected for further testing.

### 3.3 | Applicative tests on aged filter paper

Further tests were carried on the same aged filter paper (AP), whose mechanical properties before and after the aging are reported in Table 4. It is worth noting that, for these tests, we chose a safer to the artworks applicative procedure: in fact, all the tested treatments were dispersed in isopropanol, which is a solvent commonly used



**FIGURE 4** (a) Ultimate tensile strength of aged filter paper before and after treatment. (b) Elongation at rupture of aged filter paper before and after treatment. (c) pH of aged filter paper before and after treatment. (d) Bursting strength of aged filter paper before and after treatment

in conservation practice and grants a better compatibility with most of the original compounds commonly found in cellulosic artworks with respect to water, which, as previously stated, is also known to affect the mechanical properties of paper.<sup>50,51</sup> In addition to that, the treatments were applied by spraying, which, differently from the brush, does not imply a contact with the surface to be treated and it is therefore deemed safer to the artifacts.

Klucel G<sup>®</sup> (KG) belongs to the class of cellulose derivatives that are commonly used in paper conservation, and is deemed to be a good strengthening agent.<sup>52</sup> In this sense, it can be considered a state-of-the-art material for the consolidation of paper and a reference system to which new consolidating agents should be compared to. As shown in Figure 4a, b, the application of Klucel G<sup>®</sup> led to a significant increase in the Ultimate Tensile Strength (UTS) and Elasticity (E) of paper samples, but, as expected, it did not increase significantly the pH above neutrality (see Figure 4c), thus not preventing the

acid-catalyzed hydrolysis of cellulose. For what concerns the BS, even if the data are highly dispersed, a significant increase was displayed by KG (Figure 4d). This is probably due to the high molecular weight of the polymer that significantly altered the original resistance to rupture of filter paper, which is about 100 kPa. That change in the BS results in an increase of the rigidity of the paper; it is worth noting that too rigid systems are usually very fragile, as shown by the folding tests performed on NAP (see Section 3.4).

The application of the selected AT/VA copolymer (C2H) led to a significant increase in the UTS and E, as reported in Figure 4a, b, confirming the positive effect shown by the preliminary tests. In particular, changes in the UTS are equivalent to those of KG, the state-of-the-art consolidating agent of paper. Samples treated with C2H showed a neutral pH, possibly due to the presence of K<sub>2</sub>CO<sub>3</sub> from KOH residues of the synthetic procedure (see Section 2.2). Interestingly, the application of C2H

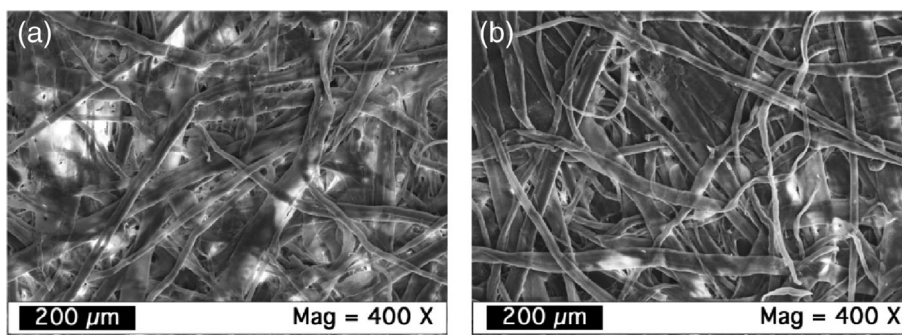


FIGURE 5 Scanning electron microscopy (SEM) pictures of AP (a) and C2H + OH (b). No significant changes due to application can be seen from these images

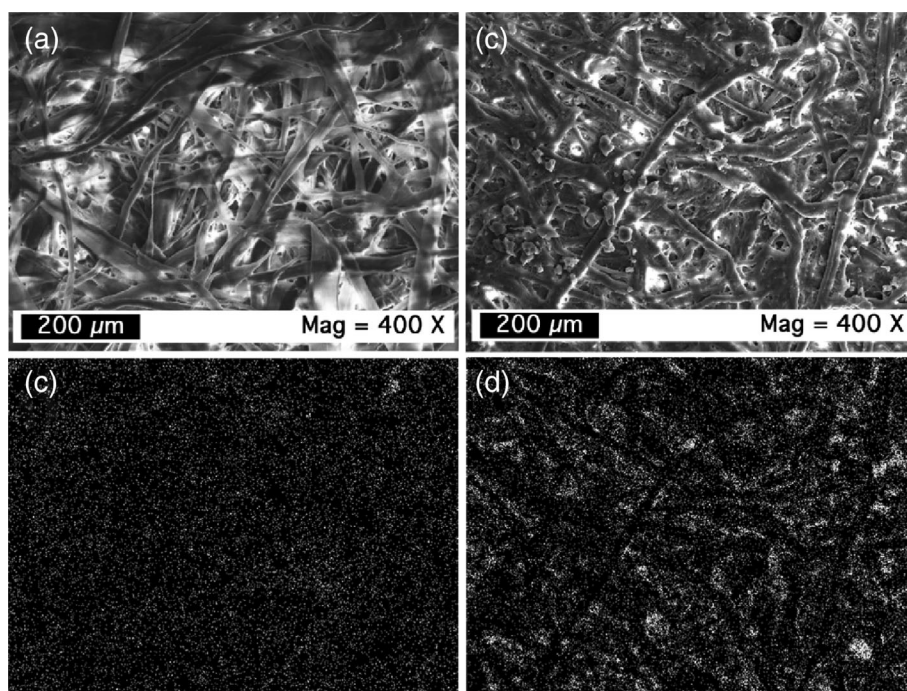


FIGURE 6 Scanning electron microscopy (SEM) picture (a) and the corresponding energy dispersive X-rays spectroscopy (EDX) map of calcium (b) of C2H + OH sample. SEM picture (c) and the corresponding EDX map of calcium (d) of NAP sample treated with the combined treatment (C2H + OH)

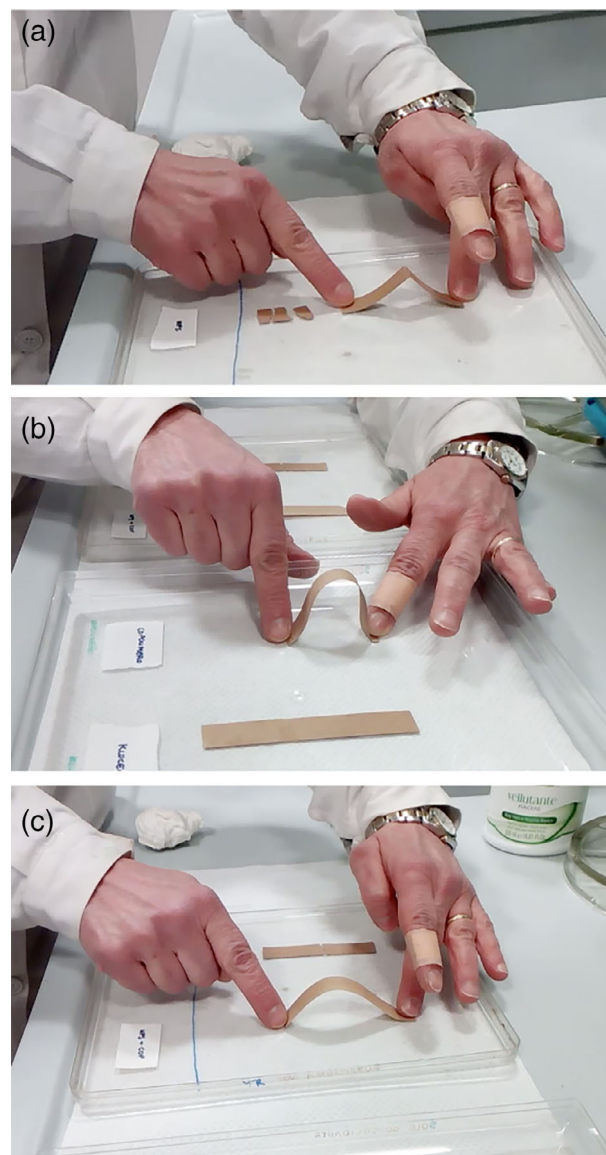


allows for the recovery of the original resistance to rupture of filter paper, expressed in terms of BS, thus preventing the main drawback shown by Klucel G<sup>®</sup> in this study, which is the notable alteration of this property, which may increase the rigidity, and consequently fragility, of treated paper. On the basis of these experimental data, it can thus be concluded that the performance of the biopolymer C2H are comparable, or even better, to those of the reference material Klucel G<sup>®</sup>.

On degraded and acidic paper, the application of a sole strengthening (C2H) agent cannot prevent further depolymerization; on this material, the use of an alkaline compound (OH), possibly leading to the formation in the cellulose matrix of the so-called alkaline reserve, which act against reoccurring acidity,<sup>53</sup> is advisable. To this aim, a combined treatment (C2H + OH) was applied on filter paper, as described in Section 2.6. The presence of alkaline particles significantly increased the pH of samples without affecting the beneficial effect of the copolymer on the mechanical properties (UTS and E). The application of the sole calcium hydroxide nanoparticles dispersion only slightly increased the UTS and the E of samples (see Figure 4a, b). In this regard, the application of the combined treatment provides the neutralization of the present acidity, the protection against reoccurring acidity and the reinforcement of the original material.

Interestingly, the combined treatment (C2H + OH), showed an increased BS of about 20% with respect to aged paper, while both the application of the sole alkaline nanoparticles or of the sole C2H increased the BS of about 10%. This synergistic effect might be explained as follows: the application of nanoparticles over the paper decreased the wettability of the surface, due to the formation of calcium carbonate upon carbonation, which is less hydrophilic than cellulose; this might result in a partial hampering of the penetration of the strengthening agent, which favors, in turn, its deposition on the surface. This might be responsible for an increase resistance to the pressure induced by the rubber diaphragm.

The application of the biopolymer C2H, alone or in combination with alkaline nanoparticles, did not significantly alter the appearance of filter paper nor at the macroscopic level ( $\Delta E^* = 3.4$ , close to the to the threshold of a color difference perceivable by the naked eye<sup>49</sup>), neither at the microscopic level, as clearly shown in the SEM pictures reported in Figure 5. In fact, from SEM pictures, the presence of the newly developed strengthening agent and of alkaline nanoparticles is not manifested. This is probably due to the high porosity of filter paper, which allows the treatment to penetrate deeply and homogeneously inside the cellulosic matrix. The uniform distribution of calcium hydroxide nanoparticles is shown in Figure 6, where a SEM picture of sample C2H + OH, together with



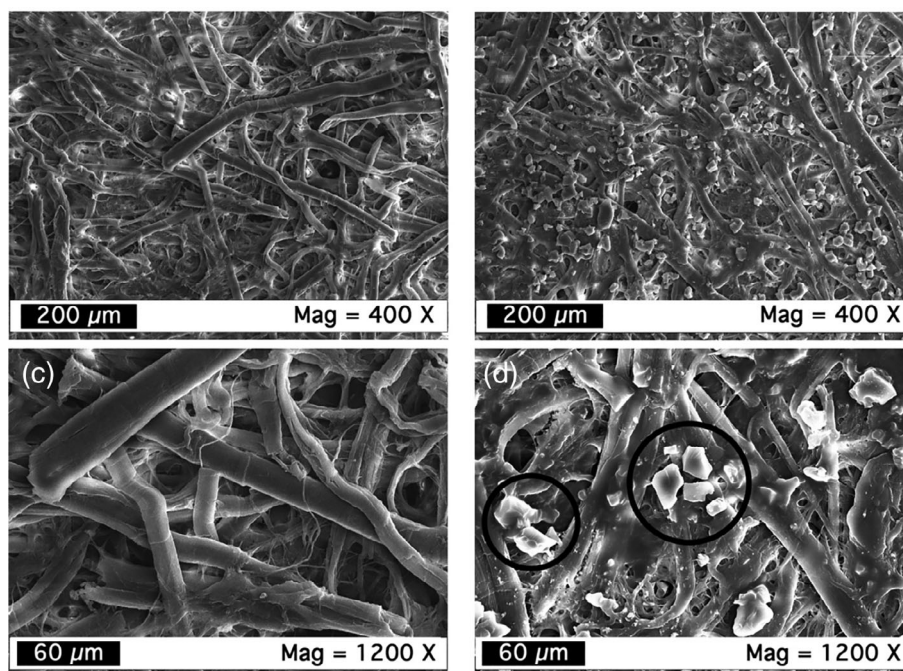
**FIGURE 7** Applicative tests on naturally aged paper (NAP): (a) NAP sample treated with alkaline nanoparticles; (b) NAP sample treated with the AT/VA copolymer; (c) NAP sample treated with nanoparticles and copolymer [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

the corresponding EDX map of calcium is reported. The white dots in the EDX map are due to the presence of nanoparticles. The same map was acquired on AP samples, showing no traces of calcium, as expected in pure filter paper (data not shown).

### 3.4 | Applicative tests on NAP

The same treatments selected to be applied on artificially aged filter paper were tested on a paper sheet from the beginning of 19th century, which, due to the low pH

**FIGURE 8** Scanning electron microscopy (SEM) pictures of NAP before (a–c) and after treatment with the newly developed strengthening agent (b–d). Black circles in D highlight the presence of polymer aggregates on the surface of the treated sample



(about 4), has a DP of about 300 and, consequently, is very fragile.

The application of C2H on discolored NAP, led to color change almost imperceptible by naked eyes, that is,  $\Delta E^* = 1.9$ .

Each sample was subjected to mechanical stress by performing manually repeated bending and straightening. All samples were bent 10 consecutive times and held in the maximum flexion position for 10 s. The test was repeated on fragments of different lengths and have been documented with videos and photos (see Figure 7). The untreated NAP sample and the one treated with nanoparticles broke at the point of maximum flexion, after only two flexions. The NAP sample treated with AT/VA copolymer broke at the tenth flexion but at the end of the strip where it was held by the operator. No break was observed at the point of maximum flexion. A similar behavior was shown by the sample treated with nanoparticles and copolymer, which did not break at the point of maximum flexion even after 10 folds. The specimen treated with Klucel G<sup>®</sup> broke right after the treatment, during manipulation, and after the first flexion, because of its excessive rigidity.

SEM pictures, reported in Figure 8, confirmed that the NAP was produced using rags; in fact, as clearly noticeable in Figure 8c, the cellulose fibers have irregular widths (10–30 μm) and show several transverse defects, also known as *nodes*.<sup>54,55</sup> These features are typical of flax or hemp, two natural materials produced from annual plants, which were commonly used to obtain rags or textiles.

On NAP, the presence of the polymer can be clearly seen from SEM pictures, reported in Figure 8b, d. In fact, the copolymer forms micron-sized aggregates on cellulose fibers and films over the surface, as shown in Figure 8-D, probably due to the lower porosity of paper. The preliminary treatment of paper with alkaline nanoparticles led to a more homogenous distribution of the strengthening agent over the paper surface (see Figure 6c). This is probably due to the fact that the presence of nanoparticles decreases the wettability of the surface, partially hampering the penetration of the strengthening agent and favoring its deposition on the surface. At the considered scale, calcium hydroxide nanoparticles are well-distributed, especially on paper porosity, and did not form clusters or micron-sized aggregates, as shown in the EDX map of calcium (Figure 6d).

## 4 | CONCLUSIONS

The synthesis of a new class of copolymers with units of vinyl alcohol and allyl  $\alpha,\alpha'$ -trehalose was optimized to investigate them as strengthening agents for severely degraded paper. Different molar ratios between monomers were tested to find the best composition for paper treatment. These biomaterials are obtained from renewable sources with a synthetic procedure that takes into account the principles of Sustainable Chemistry.

The characterization of the reaction products clearly shows the successful polymerization of the systems, and also allow us to evaluate the final ratio between monomers



in the biopolymers. Due to the reactivity of the allyl group, the presence of allyl  $\alpha,\alpha'$ -trehalose partially hampered the VAc conversion leading to a final vinyl alcohol/allyl  $\alpha,\alpha'$ -trehalose ratio slightly different from what expected. Nevertheless, all the obtained formulations were successfully applied during preliminary tests on aged filter paper in a water/isopropanol mixture, showing a good consolidating effect. The presence of  $\alpha,\alpha'$ -trehalose was shown to be effective in increasing the compatibility of the copolymers to the original cellulose network, also contributing to make them soluble in solvents or solvents mixture less polar than water that are more respectful to paper documents and drawings, which are usually highly sensitive to neat water. On the basis of these preliminary results, one of the new copolymers was selected for further testing, conducted with an applicative procedure safer to the artworks. In terms of mechanical properties, that is, tensile strength, elongation, and bursting resistance, comparable or better results than with a state-of-the-art method, that is, a commercial hydroxypropyl cellulose, were achieved. The selected strengthening treatment was also compatible with a deacidification treatment based on alkaline nanoparticle dispersed in ethanol. This two-step procedure potentially allows for hampering the main degradation pathway of cellulose, that is, acid-catalyzed hydrolysis of glycosidic bonds, and for recovering to some extent the original mechanical properties of paper. Successful tests were also performed on NAP documents from the beginning of 19th century, demonstrating that the newly developed copolymer can be fruitfully used for the strengthening of fragile cellulose-based artworks.

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## CONFLICT OF 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.

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## REFERENCES

- [1] D. Fengel, G. Wegener, *Wood: Chemistry, Ultrastructure, Reactions*, Walter De Gruyter, Berlin and New York **1984**.
- [2] T. V. Dobrodskaia, P. A. Egoyants, V. K. Ikonnikov, N. D. Romashenkova, S. A. Sirotnin, S. A. Dobrusina, N. I. Podgornaya, *Russ. J. Appl. Chem.* **2017**, *2004*, 77.
- [3] M. Strlič, J. Kolar Eds., *Ageing and Stabilization of Paper*, National and University Library, Ljubljana, Slovenia **2005**.
- [4] J. Wouters, *Science* **2008**, *322*, 1196.
- [5] W. Yanjuan, F. Yanxiong, T. Wei, L. Chunying, *J. Cult. Herit.* **2013**, *14*, 16.
- [6] M. Afsharpour, M. Hadadi, *J. Cult. Herit.* **2014**, *15*, 569.
- [7] L. Fan, M. M. Gharpuray, Y.-H. Lee, *Cellulose Hydrolysis*, Springer Berlin Heidelberg, Berlin, Heidelberg **1987**, p. 121.
- [8] L. Lundgaard, W. Hansen, D. Linhjell, T. Painter, *Power Deliv. IEEE Trans.* **2004**, *19*, 230.
- [9] N. Banait, W. Jencks, *J. Am. Chem. Soc.* **1991**, *113*, 7951.
- [10] R. Giorgi, L. Dei, C. Schettino, P. Baglioni, in *Preprint of IIC Baltimore Congress 2002, Works of Art on Paper, Books, Documents and Photographs: Techniques and Conservation* (Eds: V. Daniels, A. Donnithorne, P. Smith), International Institute for Conservation, Baltimore **2002**, p. 69.
- [11] S. Sequeira, C. Casanova, E. Cabrita, *J. Cult. Herit.* **2006**, *7*, 264.
- [12] E. Stefanis, C. Panayiotou, *Restaurator* **2007**, *28*, 185.
- [13] E. Stefanis, C. Panayiotou, *Restaurator* **2008**, *29*, 125.
- [14] E. Stefanis, C. Panayiotou, *Restaurator* **2010**, *31*, 19.
- [15] A. Wójciak, *Restaur. Int. J. Preserv. Libr. Arch. Mater.* **2015**, *36*, 3.
- [16] G. Poggi, M. C. Sistach, E. Marin, J. F. Garcia, R. Giorgi, P. Baglioni, *J. Cult. Herit.* **2016**, *18*, 250.
- [17] G. Poggi, R. Giorgi, A. Mirabile, H. Xing, P. Baglioni, *J. Cult. Herit.* **2017**, *26*, 44.
- [18] R. Giorgi, D. Chelazzi, P. Baglioni, *Langmuir* **2005**, *21*, 10743.
- [19] A. V. Chadwick, E. J. Schofield, A. M. Jones, G. Cibir, J. F. W. Mosselmans, *Solid State Ionics* **2012**, *225*, 742.
- [20] G. Poggi, N. Toccafondi, D. Chelazzi, P. Canton, R. Giorgi, P. Baglioni, *J. Colloid Interface Sci.* **2016**, *473*, 1.
- [21] F. Andriulo, S. Braovac, H. Kutzke, R. Giorgi, P. Baglioni, *Appl. Phys. A: Mater. Sci. Process.* **2016**, *122*, 322.
- [22] J. H. Stoner, R. Rushfield, *Conservation of Easel Paintings*. Routledge, London **2012**.
- [23] S. Titus, R. Schneller, E. Huhsmann, U. Hähner, G. Banik, *Restaurator* **2009**, *30*, 16.
- [24] P. Ackroyd, A. Phenix, C. Villers, *Conserv.* **2002**, *26*, 14.
- [25] J. Tétreault, E. Stamatopoulou, *Stud. Conserv.* **1997**, *42*, 141.
- [26] M. Lazzari, O. Chiantore, *Polymer (Guildf)* **2000**, *41*, 6447.
- [27] J. M. Parrent, *Stud. Conserv.* **1985**, *30*, 63.
- [28] A. Kennedy, E. R. Pennington, *Stud. Conserv.* **2014**, *59*, 194.
- [29] M. Seki, N. Sonoda, S. Hidaka, T. Morita, T. Okayama, *Restaurator* **2010**, *31*, 31.
- [30] G. Cipriani, A. Salvini, P. Baglioni, E. Bucciarelli, *J. Appl. Polym. Sci.* **2010**, *118*, 2939.
- [31] G. Cipriani, A. Salvini, M. Fioravanti, G. Di Giulio, M. Malavolti, *J. Appl. Polym. Sci.* **2013**, *127*, 420.
- [32] R. Oliva, F. Albanese, G. Cipriani, F. Ridi, D. Giomi, M. Malavolti, L. Bernini, A. Salvini, *J. Polym. Res.* **2014**, *21*, 496.
- [33] A. Papacchini, M. R. Telaretti Leggeri, L. Zucchini, M. A. Ortenzi, F. Ridi, D. Giomi, A. Salvini, *R. Soc. Open Sci.* **2018**, *5*, 171313.

- [34] A. Papacchini, S. Dominici, G. Di Giulio, M. Fioravanti, A. Salvini, *J. Cult. Herit.* **2019**, *40*, 49.
- [35] A. D. Elbein, *Glycobiology* **2003**, *13*, 17R.
- [36] N. Teramoto, N. Sachinvala, M. Shibata, *Molecules* **2008**, *13*, 1773.
- [37] J. A. Galbis, M. D. G. García-Martín, M. V. de Paz, E. Galbis, *Chem. Rev.* **2016**, *116*, 1600.
- [38] A. J. Varma, J. F. Kennedy, P. Galgali, *Carbohydr. Polym* **2004**, *56*, 429.
- [39] G. Poggi, N. Toccafondi, L. N. Melita, J. C. Knowles, L. Bozec, R. Giorgi, P. Baglioni, P. Baglioni, *Appl. Phys. A: Mater. Sci. Process.* **2014**, *114*, 685.
- [40] ASTM D828-97 Standard Test Method for Tensile Properties of Paper and Paperboard Using Constant-Rate-of-Elongation Apparatus **2002**.
- [41] TAPPI T494 Tensile properties of paper and paperboard (using constant rate of elongation apparatus) **2006**.
- [42] UNI EN ISO 1924-2 Paper and board - Determination of tensile properties - Part 2: Constant rate of elongation method (20 mm/min) **2009**.
- [43] UNI EN ISO 2758 Paper - Determination of bursting strength **2014**.
- [44] UNI 8282 Cellulose in dilute solutions - determination of limiting viscosity number - method in cupri-ethylene-diamine (CED) solution - equivalent to the ISO standard 5351/1 **1994**.
- [45] A.-L. Dupont, G. Mortha, *J. Chromatogr. A* **2004**, *1026*, 129.
- [46] P. Calvini, A. Gorassini, A. L. Merlani, *Cellulose* **2008**, *15*, 193.
- [47] C. H. Stephens, P. M. Whitmore, H. R. Morris, M. E. Bier, *Biomacromolecules* **2008**, *9*, 1093.
- [48] G. Sharma, W. Wu, E. N. Dalal, *Color Res. Appl.* **2005**, *30*, 21.
- [49] R. F. Witzel, R. W. Burnham, J. W. Onley, *J. Opt. Soc. Am.* **1973**, *63*, 615.
- [50] A. Casoli, P. Cremonesi, C. Isca, R. Groppetti, S. Pini, N. Senin, *Cellulose* **2027**, *2013*, 20.
- [51] C. Isca, L. Fuster-López, D. J. Yusá-Marco, A. Casoli, *Cellulose* **2015**, *22*, 3047.
- [52] O. Nechyporchuk, K. Kolman, A. Bridarolli, M. Odlyha, L. Bozec, M. Oriola, G. Campo-Francés, M. Persson, K. Holmberg, R. Bordes, *Carbohydr. Polym.* **2018**, *194*, 161.
- [53] S. Zervos, I. Alexopoulou, *Cellulose* **2015**, *22*, 2859.
- [54] M. Aslan, G. Chinga-Carrasco, B. F. Sørensen, B. Madsen, *J. Mater. Sci.* **2011**, *46*, 6344.
- [55] R. K. Nayak, R. Padhye, S. Fergusson, In *Handbook of Natural Fibres*. Woodhead Publishing Limited, Cambridge **2012**.

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