

Cellulose as a Renewable Resource for the Synthesis of Wood Consolidants

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Received 22 June 2009; accepted 14 April 2010

DOI 10.1002/app.32634

Published online 30 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Crosslinkable cellulose ethers as allyl cellulose, allyl carboxymethyl cellulose, and allyl *n*-hydroxypropyl cellulose were synthesized and characterized, and their use as consolidating agents for waterlogged wood was studied. For this kind of application, structural properties similar to those of wood's polysaccharide components are desired in the design stage of new consolidants. The choice to synthesize cellulose ethers was determined from the possibility of using cellulose as the starting material because of its large availability in nature, biocompatibility, and low cost. In addition, cellulose ethers are quite easy to obtain, and they can have different properties, depending on the nature and the amount of the functional

groups introduced. For this purpose, a cellulose with a lower degree of polymerization was also used for the synthesis of related cellulose ethers. By means of Fourier transform infrared spectroscopy, the affinity of the cellulose derivatives for degraded lignin flours was detected. The preliminary results of this study show that these polysaccharide compounds may be proposed as wood consolidating agents. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2939–2950, 2010

Key words: crosslinking; functionalization of polymers; polysaccharides; renewable resources; water-soluble polymers

INTRODUCTION

In the past, many investigations have been concerned with several compounds and methods for the treatment of waterlogged wood.^{1–5} Out of the various compounds, poly(ethylene glycol) compounds with various molecular weights^{6–8} have provided the greatest benefits. Several problems have appeared consequent to the use of poly(ethylene glycol) because of its hygroscopicity, its relatively high cost, and the chromatic alteration of the wood manufacturing products,^{9–11} thus, the study of different wood consolidants is required.

The use of renewable resources appears to be an interesting alternative to the production of new polymers that would be useful in many fields of application. Cellulose is one of the most important natural polymers. From the current point of view, it is also the most common organic polymer and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products.¹² For these reasons, several synthetic cellulose derivatives are of great industrial importance, and the chemistry

of cellulose derivatization has been intensively studied in recent decades to obtain a range of products having different chemical and physical properties.¹³ In detail, the synthesis of cellulose ethers is an important aspect of commercial cellulose derivatization. Most cellulose ethers are water-soluble polymers, and some types are also soluble in organic solvents: in many cases, their water solubility can be controlled to a certain extent by the combination of different ether groups, the degree of substitution (DS), and the distribution of the substituents.¹⁴ They have a high chemical stability and are toxicologically innocuous. Because of these positive features, cellulose ethers are used in several industrial applications, such as in the building materials market, the pharmaceutical and cosmetics industries, additives to drilling fluids for consistency control, and stabilizers for beverages.¹⁵

Some of these compounds, such as methyl cellulose and hydroxypropyl cellulose (HPC), have also been used in the field of waterlogged wood conservation.^{16,17} However, several problems have been observed because of their high molecular weights, which lead to poor penetration ability, and to their easy biological deterioration. In this article, we report the syntheses and characterization of water-soluble and crosslinkable cellulose ethers, both in high and low degree of polymerization (DP) versions, as consolidating agents for waterlogged wood.

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To verify their affinity for degraded wood material, the amount of polymer absorbed on the lignin flours was evaluated with Fourier transform infrared (FTIR) spectroscopy. The introduction of different groups on the cellulose backbone allowed the modification of the affinity of the macromolecule for water or wood and could reduce the biological deterioration of the material. In particular, the carboxymethyl and *n*-hydroxypropyl groups were used to increase the water solubility and the affinity for wood of the consolidant. The allyl group was introduced to produce a crosslinkage and to reduce the mobility and biological deterioration of the consolidant. The molecular size reduction of the starting cellulose ether could lead to a greater penetration of the consolidant into the wooden structure. For this purpose, it was very important to consider and evaluate the molecular dimensions of the consolidant in relationship to its capacity to penetrate into the pores of the wood manufacturing products that we were trying to restore. For this reason, a compound with a molecular weight that was too high would show a poor ability to penetrate inside wood pores and would result in a poor wood consolidant, although it could be suitable for superficial protective action. On the other hand, a compound with a high molecular weight could certainly guarantee an improvement in the mechanical properties of restored wood so that the process of consolidation is more effective. Preliminary tests on the application of the synthesized polymers on strongly degraded wood flour samples were performed to verify their ability to penetrate inside cellular walls and to determine if their crosslinking potential would permit anchorage of the macromolecule inside the wood structure.

EXPERIMENTAL

Materials

Cellulose microcrystalline, carboxymethyl cellulose (CMC), lithium chloride, allyl bromide, 3-chloro-1-propanol, 3-bromo-1-propanol, and sodium chloroacetate were purchased from Aldrich Co. (St. Louis, MO) *N,N*-Dimethylacetamide (DMAc) and ethanol were purchased from Fluka Co. (St. Louis, MO) Trichloromethane, diethyl ether, hydrogen chloride, sulfuric acid, and anhydrous sodium hydroxide were purchased from Riedel-De Haën (Seelze, Germany). Deuterated solvents (CDCl₃, D₂O) were purchased from Aldrich. All of the chemicals were reagent grade and were used without further purification.

Instruments

¹H-NMR, ¹³C-NMR, gradient field COrrrelation Spectroscopy (gCOSY), and gradient field Heteronuclear

Single Quantum Coherence (gHSQC) spectra were recorded with a Varian (Palo Alto, CA) Mercury Plus 400 spectrometer, working at 399.921 MHz. All spectra are reported in parts per million and refer to tetramethylsilane (TMS) as an internal standard. Spectral elaboration was subsequently executed with Mestre-C 4.3.2.0 (Mestrelab Research, Santiago de Compostela, Spain) software.

FTIR spectra were recorded with a PerkinElmer (Waltham, MA) Spectrum BX model and elaborated with Spectrum (PerkinElmer, Waltham, MA) version 3.02.02 software. The solutions were analyzed with KBr or CaF₂ round cell windows after deposition and evaporation of the solvent. The spectra of the solid samples were recorded as KBr pellets.

A capillary viscometer was used to evaluate the DP. The cellulose sample (60 mg) was added to an aqueous solution of cupriethylenediamine (50 mL, 0.5M), and the mixture was stirred at room temperature for 3 h until the sample was completely dissolved. The solution was allowed to rest at 25°C in a thermostatic bath for 1 h and was then moved into the capillary viscometer to perform the analysis.¹⁸

Synthesis

Cellulose dissolution

The procedure reported by McCormick et al.¹⁹ was used and was modified as follows: into a dry 500-mL, two-necked flask equipped with a vacuum/nitrogen inlet/outlet and a reflux condenser, 500 mg of cellulose microcrystalline (or hydrolyzed cellulose) and 20 mL of a LiCl/DMAc solution (6% w/w) were added under a nitrogen atmosphere. The mixture was stirred at 120°C for 90 min; then, it was allowed to cool at room temperature until it was clear.

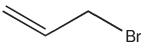
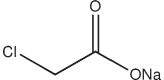
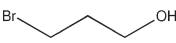
Cellulose hydrolysis

Cellulose microcrystalline (1 g) and hydrogen chloride (2N, 20 mL) were introduced into a 50-mL flask. The mixture was stirred at 80°C for 24 h, allowed to cool at room temperature, and then centrifuged. The solid residue was washed four to five times with demineralized water until the pH of the solution was neutral and dried *in vacuo* and then in an oven at 70°C for 16 h. The solid product (0.91 g) was added to 20 mL of acetone and stirred for 1 h, filtered on a Gooch funnel, washed with acetone, and then dried *in vacuo* (0.87 g).

Allyl cellulose (1)[zaq noq11

A modified version of the synthetic procedure reported by Lin and Huang²⁰ was used: into a dry 100-mL, two-necked flask equipped with a vacuum/nitrogen inlet/outlet and a reflux condenser, powdered sodium hydroxide (1.5 g, 37.7 mmol) was

TABLE I
Syntheses of the Lower DP Cellulose Ethers: Reagent Amounts

	Cellulose	NaOH			
Allyl carboxymethyl cellulose (3)	0.500 g	1.000 g (25 mmol)	1.010 g (8.3 mmol)	0.490 g (4.2 mmol)	—
Allyl carboxymethyl cellulose (4)	0.175 g	0.330 g (8.3 mmol)	0.168 g (1.4 mmol)	0.326 g (2.8 mmol)	—
Allyl <i>n</i> -hydroxypropyl cellulose (6)	0.175 g	0.330 g (8.3 mmol)	0.363 g (3.0 mmol)	—	0.195 g (1.4 mmol)
Allyl <i>n</i> -hydroxypropyl cellulose (7)	0.175 g	0.330 g (8.3 mmol)	0.168 g (1.4 mmol)	—	0.389 g (2.8 mmol)

added under continuous stirring to 10 mL of a LiCl/DMAc (6% w/w) cellulose solution under a nitrogen atmosphere, and the mixture was heated at 80°C for 40 min. After cooling at room temperature, allyl bromide (3.26 mL, 37.7 mmol) was added, and the reaction mixture was allowed to react at 80°C for 5 h. The mixture was then added to 120 mL of water and extracted five times with chloroform (10 mL). After vacuum distillation, the oily product obtained was washed with water, and the resulting white solid was filtered on a Gooch funnel, washed again with water, and dried *in vacuo* at 60°C (196 mg, DS = 3, 57.0% yield).

¹H-NMR (CDCl₃, 400 MHz, ppm): 3.13, 3.35, 3.68, 3.83, 4.01 (m, 5H, H₂–H₆ cellulose backbone); 4.21 (m, 2H, –CH₂–O–allyl); 4.40 (m, 1H, H₁ cellulose backbone); 5.18 (m, 2H, CH₂=CH–CH₂–); 5.91 (m, 1H, CH₂=CH–CH₂–). ¹³C-NMR (CDCl₃, 100 MHz, ppm): 72.2, 73.9, 74.2, 75.1 (C₂–C₆ cellulose backbone); 81.6 (–CH₂–O–allyl); 103.2 (C₁ cellulose backbone); 116.7 (CH₂=CH–CH₂–); 135.5 (CH₂=CH–CH₂–).

Allyl carboxymethyl cellulose (2)

Into a dry 100-mL, two-necked flask equipped with a vacuum/nitrogen inlet/outlet and a reflux condenser, powdered sodium hydroxide (0.66 g, 16.6 mmol) was added under continuous stirring to 20 mL of a LiCl/DMAc (6% w/w) cellulose solution under a nitrogen atmosphere, and the mixture was heated at 80°C for 40 min. After cooling at room temperature, a solution of allyl bromide (0.72 mL, 8.3 mmol) in DMAc (10 mL) was added in 10 min through a dropping funnel, and the mixture was allowed to react at 70°C for 18 h. Powdered sodium hydroxide (0.34 g, 8.4 mmol) was added, and the mixture was heated at 80°C for 40 min. After cooling at room temperature, a solution of sodium chloroacetate (0.49 g, 4.2 mmol) in DMAc (20 mL) was added, and the mixture was allowed to react at 70°C for 72 h. The reaction mixture was then added to 250 mL of ethanol, and the precipitate obtained was filtered through a Gooch funnel and washed with ethanol. The crude white yellow solid was dried in oven at 80°C, and 1.08 g of product was recovered. The solid was dispersed in 50 mL of demineralized

water, and HCl (1N) was added until pH 3 was reached. The dispersion was then washed three times with diethyl ether. Sodium hydrogen carbonate was added to the aqueous phase until pH 10 was reached; then, the dispersion was added to 250 mL of ethanol. The precipitate obtained was centrifuged, washed three times with ethanol, and dried *in vacuo* (0.42 g, DS_{allyl} = 1, DS_{carboxymethyl} = 1, 48.7% yield).

¹H-NMR (D₂O, 400 MHz, ppm): 3.39, 3.68, 3.77, 3.84, 4.01 (m, 5H, H₂–H₆ cellulose backbone); 4.13 (m, 2H, –CH₂–O–allyl); 4.30 (m, 2H, –CH₂–COO[–]); 4.57 (m, 1H, H₁ cellulose backbone); 5.35 (m, 2H, CH₂=CH–CH₂–); 6.01 (m, 1H, CH₂=CH–CH₂–). ¹³C-NMR (CDCl₃, 100 MHz, ppm): 69.6–81.4 (C₂–C₆ cellulose backbone, –CH₂–O–allyl, –CH₂–COO[–]), 102.2 (C₁ cellulose backbone), 118.3 (CH₂=CH–CH₂–), 133.7 (CH₂=CH–CH₂–); 177.0 (–COO[–]).

Allyl carboxymethyl cellulose (lower DP; 3 and 4)

Allyl carboxymethyl cellulose ethers (lower DP) with two different DS values were synthesized with hydrolyzed cellulose as a starting material. For the synthetic procedure, see the synthesis of allyl carboxymethyl cellulose (2). For the reactions conditions and data, see Tables I and II.

Allyl *n*-hydroxypropyl cellulose (5)

Into a dry 100-mL, two-necked flask equipped with a vacuum/nitrogen inlet/outlet and a reflux condenser, powdered sodium hydroxide (0.64 g, 16 mmol) was added under continuous stirring to 20 mL of a LiCl/DMAc (6% w/w) cellulose solution under a nitrogen atmosphere, and the mixture was heated at 80°C for 40 min. After cooling at room temperature, a solution of 3-bromo-1-propanol (0.72 mL, 8 mmol) in DMAc (15 mL) was added, and the mixture was allowed to react at 70°C for 18 h. Powdered sodium hydroxide (0.36 g, 9 mmol) was added, and the mixture was heated at 80°C for 40 min. After cooling at room temperature, a solution of allyl bromide (0.39 mL, 4.5 mmol) in DMAc (15 mL) was added, and the mixture was allowed to react at 70°C for 5 h. The reaction mixture was then added to 250 mL of ethanol, and the precipitate

TABLE II
Syntheses of the Lower DP Cellulose Ethers: DS and Yield Values

	DS _{allyl}	DS _{carboxymethyl}	DS _{n-hydroxypropyl}	Product amount (g)	Yield (%)
Allyl carboxymethyl cellulose (3)	0.5	0.5	—	0.410	60.0
Allyl carboxymethyl cellulose (4)	0.4	1.1	—	0.187	65.0
Allyl <i>n</i> -hydroxypropyl cellulose (6)	0.7	—	0.2	0.087	39.5
Allyl <i>n</i> -hydroxypropyl cellulose (7)	0.3	—	0.7	0.098	42.5

obtained was filtered through a Gooch funnel, washed with ethanol, and dried *in vacuo* (1.2 g). The white solid was added to 100 mL of ethanol and kept under continuous stirring at room temperature for 3 h. After filtration, the solid was dried *in vacuo* (0.62 g, DS_{allyl} = 0.2, DS_{n-hydroxypropyl} = 0.6, 98.0% yield).

¹H-NMR (D₂O, 400 MHz, ppm): 1.87 (m, 2H, —O—CH₂—CH₂—CH₂—OH); 3.23 (m, 1H, H₂ cellulose backbone); 3.68 (m, 4H, —O—CH₂—CH₂—CH₂—OH); 3.83, 3.96, 3.98, 4.01 (m, 4H, H₃—H₆ cellulose backbone); 4.12 (m, 2H, —CH₂—O—allyl); 4.54 (m, 1H, H₁ cellulose backbone); 5.33 (m, 2H, CH₂=CH—CH₂—); 5.99 (m, 1H, CH₂=CH—CH₂—).

Allyl *n*-hydroxypropyl cellulose (lower DP; 6 and 7)

Allyl *n*-hydroxypropyl cellulose ethers (lower DP) with two different DS values were synthesized with hydrolyzed cellulose as a starting material. For the synthetic procedure, see the synthesis of allyl *n*-hydroxypropyl cellulose (5). For the reactions conditions and data, see Tables I and II.

Small-angle X-ray scattering (SAXS)

A water colloidal dispersion of the cellulose ether sample was centrifuged at 1000 rpm, and the clear liquid phase was used to fill a Mark tube (diameter = 1 mm). SAXS measurements were carried out with a HECUS (Graz, Austria) SWAX-camera (Kratky) equipped with a position-sensitive detector (OED 50M) containing 1024 channels with a width of 54 μm. Cu Kα radiation with a wavelength (λ) of 1.542 Å was provided by a Seifert (Massillon, OH) ID-3003 X-ray generator (sealed-tube type), operating at a maximum power of 2 kW. A 10 μm thick Ni filter was used to remove the Cu Kβ radiation. The sample-to-detector distance was 275 mm. The volume between the sample and the detector was kept *in vacuo* during the measurements to minimize scattering from the air. The Kratky camera was calibrated in the small-angle region with silver behenate (*d* = 58.38 Å).²¹ Scattering curves were obtained in the scattering vector (**Q**) range $Q = 4\pi \sin \theta / \lambda$ between 0.009 and 0.54 Å⁻¹, where 2θ is the scattering angle. The temperature was controlled by a Peltier element with an accuracy of ±0.1°C.

We corrected all of the scattering curves for the water/empty cell contribution by considering the relative transmission factor. SAXS curves were iteratively desmeared with the procedure reported by Lake.²²

Wood flour preparation and Soxhlet extraction

We obtained oak wood sample flour by grinding the sample in an agate mortar and then passing it through a 300-μm sieve. The wood flour (116 mg) was introduced into a cellulose thimble and then placed into a Soxhlet extractor. The flask was filled with 200 mL of ethanol (95%), and after 6 h of extraction, the thimble was placed in an oven at 70°C for 24 h.

Lignin preparation: Klason procedure

The pre-extracted wood flour was added to 15 mL of sulfuric acid (72%) in a beaker and kept under continuous stirring at 0°C for 10 min. The beaker was then allowed to come back to room temperature, and the stirring was continued for 2 h. The solution was diluted to 3%, brought to the boiling point, and kept at that temperature for 4 h, with water added during the process to keep the volume constant. The solution was decanted, and the lignin residue was filtered, washed, and dried in oven at 103°C.

Lignin treatments

Treatment of lignin with CMC

In a 50-mL, round-bottom flask, oak lignin (15 mg) was kept under continuous stirring into a solution of CMC (100 mg) in demineralized water (10 mL) for 4 days at room temperature. After filtration and washing, the solid residue was dried *in vacuo* and then in oven at 60°C for 24 h (17 mg).

Treatment of lignin with allyl carboxymethyl cellulose (lower DP)

In a 25-mL, round-bottom flask, oak lignin (15 mg) was kept under continuous stirring in a colloidal dispersion of lower DP allyl carboxymethyl cellulose (3; 100 mg) in demineralized water (10 mL) for 4 days at room temperature. After centrifugation and washing, the solid residue was dried *in vacuo* and then in an oven at 60°C for 24 h (18 mg).

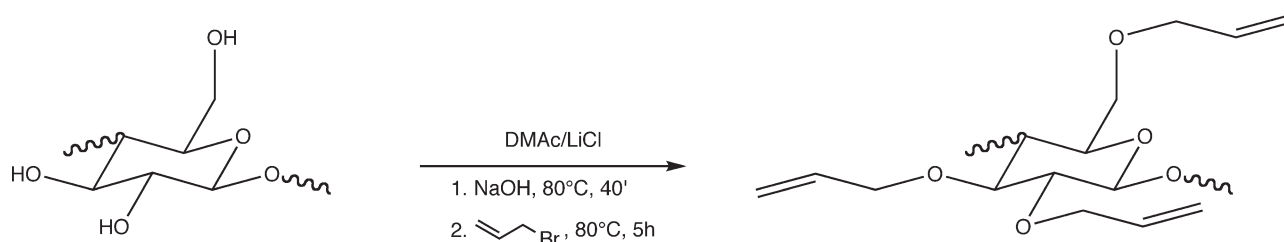


Figure 1 Allyl cellulose synthesis.

Treatment of lignin with allyl *n*-hydroxypropyl cellulose (lower DP)

In a 100-mL, round-bottom flask, oak lignin (15 mg) was kept under continuous stirring into a colloidal dispersion of lower DP allyl *n*-hydroxypropyl cellulose (7) (150 mg) in demineralized water (30 mL) for 4 days at room temperature. After centrifugation and washing, the solid residue was dried *in vacuo* and then in oven at 60°C for 24 h (18 mg).

Degraded wood treatment

An oak wood cubic sample (1 cm³, 0.259 g) recovered from an archaeological waterlogged find was used for the consolidation treatment. The relative amount of cellulose and lignin was detected with FTIR spectroscopy. In a 25-mL, screw-capped Sovirel tube (Bagneaux-sur-Loing, France), the sample was kept in a colloidal dispersion of lower DP allyl carboxymethyl cellulose (3; 2.0 g) in demineralized water (18 mL) for 20 days at room temperature. The sample was removed from the dispersion, washed with demineralized water, and dried in oven at 60°C for 24 h (0.361 g).

RESULTS AND DISCUSSION

Synthesis and characterization of the cellulose ethers

The first attempts to synthesize desired cellulose ethers were made with heterogeneous reaction conditions because of the lack of solubility of cellulose in common organic solvents or water. However, under these conditions, working with a suspension of cellulose in an aqueous solution of sodium hydroxide, we never obtained the intermediate alkali cellulose. In a second attempt, a sodium hydroxide/water/isobutyl alcohol system was used, but even with this method, the alkali cellulose was not obtained. The very low reactivity observed for cellulose etherification could be explained by the heterogeneous conditions used for these syntheses.

McCormick and Callais^{19,23,24} reported a convenient solvent system for solubilizing cellulose and carried out different reactions in it. In fact, with solutions of lithium chloride in DMAc (from 2 to 8 wt

%), a complete dissolution of cellulose was obtained, and the subsequent etherification or esterification reactions could be performed with this solution. However, sodium hydroxide was not soluble in this solvent system, so to obtain the alkali cellulose required for the subsequent etherification reactions, a stable suspension of fine powdered NaOH in DMAc/LiCl had to be prepared. A fast alkalization of cellulose hydroxyl groups was then obtained.

To reduce the mobility of the consolidant after its penetration into wood, one of the aims of this study was the synthesis of cellulose derivatives able to give crosslinking reactions. This goal was achieved by the introduction of allylic groups into the cellulose backbone. However, allyl cellulose is known to be completely soluble in chloroform and dimethyl sulfoxide but not in water. This behavior is a problem for subsequent application on waterlogged wood because the use of an organic solvent requires the replacement of water with the solvent used. In addition, this is not recommended in the field of cultural heritage conservation because of safety problems. Therefore, the next objective was to find some mixed cellulose ethers able to give crosslinking reactions but, at the same time, with a partial or complete solubility in water. The first group used to improve the water solubility was the carboxymethyl anion. In fact, the commercially most important cellulose ether, CMC, showed complete solubility in water at DS > 0.3. This property was due to the presence of anionic sodium carboxymethyl groups, which provided a greater hydrophilicity to the macromolecule. The allyl group was used to obtain a crosslinking reaction between the chains of the cellulose ether. At first, the reaction conditions used to obtain the allyl derivatives were optimized with respect to those reported in the literature for the synthesis of allyl cellulose.²⁰ In fact, this compound was obtained with the DMAc/LiCl solvent system by modification of the procedure reported by Lin and Huang;²⁰ the allyl cellulose obtained, characterized by NMR spectroscopy, was completely allylated (DS = 3) and isolated with a 57.0% yield (see Experimental section; Fig. 1).

The spectral data obtained were in agreement with the literature.²⁰ With the DMAc/LiCl solvent

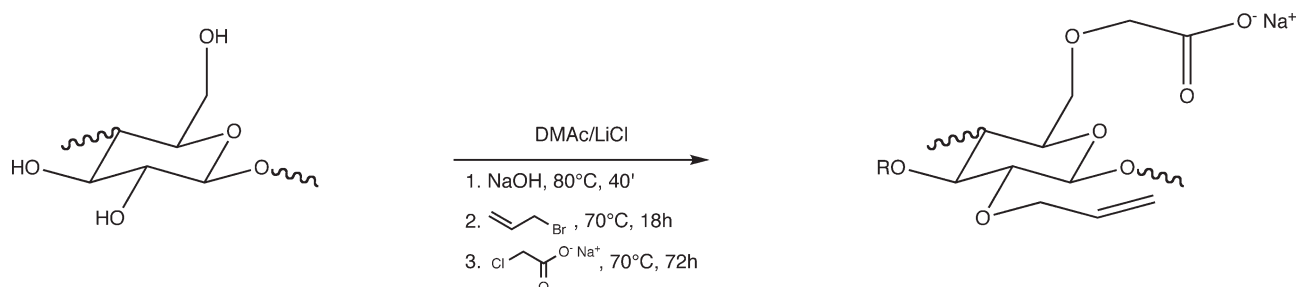


Figure 2 Allyl carboxymethyl cellulose synthesis.

system, a new cellulose derivative, allyl carboxymethyl cellulose, was then synthesized, with the introduction of two different groups into the cellulose backbone: a hydrophilic group and a crosslinkable one. The synthesis was carried out in a single step; we first obtained the allyl ether, which was not isolated to minimize reaction time and optimize workup procedures, and then added sodium chloroacetate (less reactive than allyl bromide) to obtain the mixed ether with a total DS of 2 ($\text{DS}_{\text{allyl}} = 1$, $\text{DS}_{\text{carboxymethyl}} = 1$) and a yield of 48.7% (Fig. 2).

This polymer was characterized by NMR spectroscopy. In the ^1H -NMR spectrum (Fig. 3), the signals at 4.13, 5.35, and 6.01 ppm were related to the allylic group protons ($-\text{CH}_2-$, $=\text{CH}_2$, $-\text{CH}=\text{}$), whereas the presence of the sodium carboxymethyl group was confirmed by the signal at 4.30 ppm, which was related to the methylenic protons ($-\text{CH}_2-\text{COO}^-$). The other signals in the spectrum were related to the cellulose backbone protons. Moreover, from the gCOSY spectrum, it was possible to see the correlations for the allylic group and no correlations for the

CH_2 near the carboxylic group; this confirmed the macromolecular structure. In the ^{13}C -NMR spectrum, a series of signals in the range 69.6–81.4 ppm were related to the cellulose backbone carbons (C_2 – C_6), the allylic CH_2 , and the CH_2 near the carboxylic group. At higher frequencies, the signal at 177.0 ppm confirmed the presence of the carboxylic group ($-\text{COO}^-$). The DS values of the two groups were calculated through the analysis of the ^1H -NMR spectrum (Fig. 3) with the following equation system:

$$\text{DS}_{\text{allyl}} = 7k/(1 - 2k) \quad (1)$$

$$\text{DS}_{\text{carboxymethyl}} = \text{DS}_{\text{allyl}}/2x \quad (2)$$

where DS_{allyl} is the degree of substitution of the allylic group, $\text{DS}_{\text{carboxymethyl}}$ is the degree of substitution of the sodium carboxymethyl group, k is the area of signal A ($\delta = 6.01$ ppm) divided by the area of signal B ($\delta = 3.39$ – 4.13 ppm; $\delta = 4.57$ ppm; Fig. 3), and x is the area of signal A ($\delta = 6.01$ ppm) divided by the area of signal C ($\delta = 4.30$ ppm; Fig. 3).

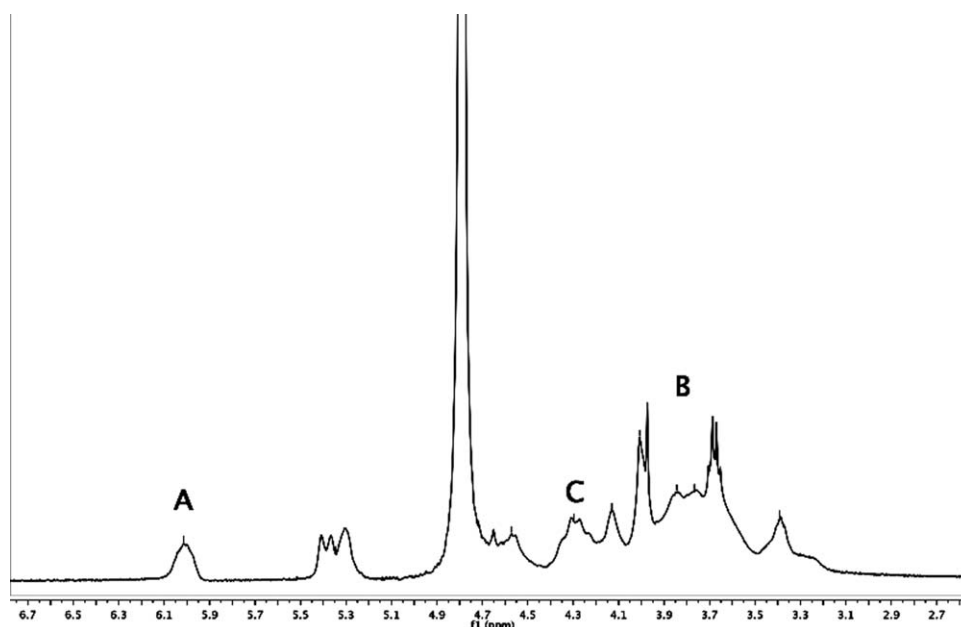


Figure 3 ^1H -NMR spectrum of allyl carboxymethyl cellulose.

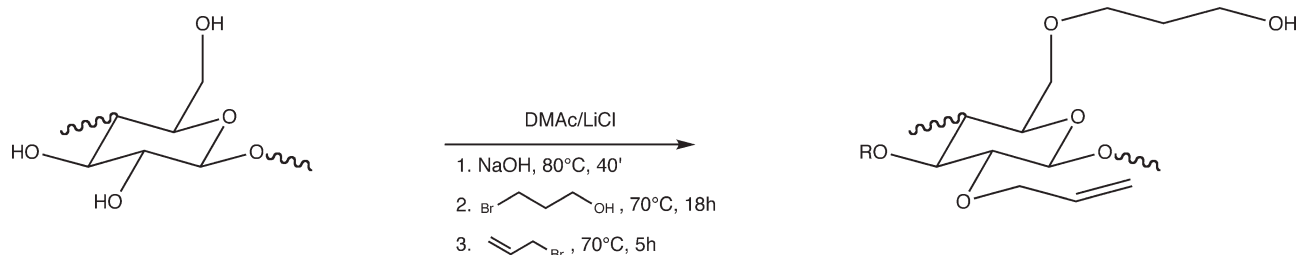


Figure 4 Allyl *n*-hydroxypropyl cellulose synthesis.

The synthesized compound was found to give a stable colloidal system in cold water. To expand the possibilities of application on waterlogged wood and to obtain more than one macromolecular compound with the desired properties of solubility and crosslinking potential, a third synthesis was designed and carried out. In this case, cellulose was functionalized with a novel, alternative hydrophilic group, the *n*-hydroxypropyl group. In fact, hydroxyalkyl ethers of cellulose, such as hydroxyethyl cellulose and HPC, are commercially relevant derivatives. They are obtained from the reaction of cellulose with ethylene oxide and propylene oxide, respectively. However, in the case of HPC, the use of propylene oxide as a reagent brought some problems related to its toxicity and hazardous nature. Moreover, its high reactivity with hydroxyl groups of cellulose could result in an uncontrolled process, which could lead to products with too high a DS. For this reason, the reagent used in the synthesis was 3-bromo-1-propanol, which was less reactive

and hazardous and led to 3-hydroxypropyl ether; when propylene oxide was used, 2-hydroxypropyl ether was obtained.

Also, in this case, the synthesis was carried out in a single step; we first obtained *n*-hydroxypropyl ether, which was not isolated. Allyl bromide was then added to the mixture, and the mixed ether was obtained with a total DS of 0.8 ($DS_{\text{allyl}} = 0.2$, $DS_{n\text{-hydroxypropyl}} = 0.6$) and a yield of 98% (Fig. 4).

In the ¹H-NMR spectrum (Fig. 5), the signals at 4.12, 5.33, and 5.99 ppm were related to the allylic group protons ($-\text{CH}_2-$, $=\text{CH}_2$, and $-\text{CH}=\text{}$, respectively), whereas the presence of the *n*-hydroxypropyl group was confirmed by signals at 1.87 ppm ($-\text{C}-\text{CH}_2-\text{C}-$) and 3.68 ppm ($\text{O}-\text{CH}_2-$). The other signals were related to the cellulose backbone protons. Moreover, from the gCOSY spectrum, it was possible to see the correlations for the allylic and *n*-hydroxypropyl groups (this one was between the two signals at 1.87 and 3.68 ppm), which confirmed the macromolecular structure. The DS values of the

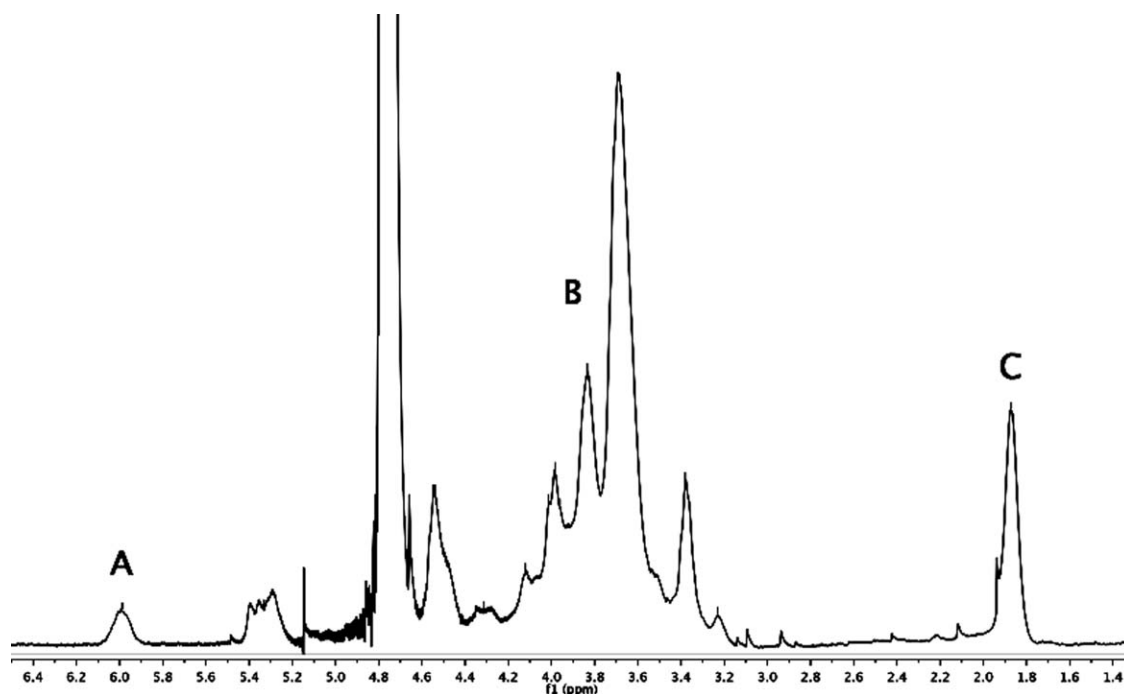


Figure 5 ¹H-NMR spectrum of allyl *n*-hydroxypropyl cellulose.

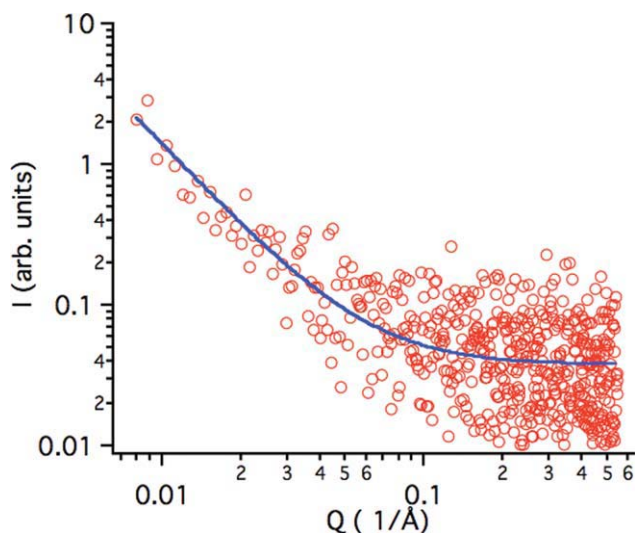


Figure 6 SAXS intensity distribution for lower DP allyl *n*-hydroxypropyl cellulose (7). The continuous line represents the best fitting with the Debye model. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

two groups were calculated through the analysis of the $^1\text{H-NMR}$ spectrum (Fig. 5) with the following equation system:

$$\text{DS}_{\text{allyl}} = k(7 + 4\text{DS}_{n\text{-hydroxypropyl}})/(1 - 2k) \quad (3)$$

$$\text{DS}_{n\text{-hydroxypropyl}} = \text{DS}_{\text{allyl}}/2x \quad (4)$$

where $\text{DS}_{n\text{-hydroxypropyl}}$ is the degree of substitution of the *n*-hydroxypropyl group, k is the area of signal A ($\delta = 5.99$ ppm) divided by the area of signal B ($\delta = 3.23\text{--}4.54$ ppm; Fig. 5), and x is the area of signal A ($\delta = 5.99$ ppm) divided by the area of signal C ($\delta = 1.87$ ppm; Fig. 5).

Also, this compound was found to give a stable colloidal system in cold water. Overall, the properties of allyl carboxymethyl cellulose and allyl *n*-hydroxypropyl cellulose seemed suitable for application as consolidants for waterlogged wood because of their similarity to wood's cellulose backbone, their hydrophilicity, and their potential crosslinking mechanism.

However, a limiting factor for their application on wood was their molecular weight. To evaluate the molecular weights of the synthesized cellulose ethers, a viscometry measurement¹⁸ on the initial microcrystalline cellulose was performed; this showed a DP of about 335 (55,000 g/mol), which was relatively high for our application field. To decrease the molecular weights and improve the penetration ability of the cellulose ethers, an acid hydrolysis reaction was carried out on the microcrystalline cellulose. With HCl at 80°C, after 24 h, a hydrolyzed cellulose was isolated. This sample was

analyzed by means of capillary viscometry and showed a DP of about 225 (36,000 g/mol). Starting from lower DP cellulose, the next step was to obtain allyl carboxymethyl cellulose and allyl *n*-hydroxypropyl cellulose with a decreased molecular weight. To obtain a library of cellulose ethers with different DS values and, consequently, different chemical properties, several syntheses were performed with various ratios of the alkylating reagents. The syntheses and workup procedures were carried out in the same way as for the higher DP derivatives to obtain lower DP allyl carboxymethyl cellulose and lower DP allyl *n*-hydroxypropyl cellulose with different DS values (Tables I and II). The lower DP cellulose ethers were characterized through NMR spectroscopy. All synthesized compounds were found to give stable colloidal systems in cold water.

To evaluate the particle dimensions of the lower DP cellulose ethers, a water colloidal dispersion of lower DP allyl *n*-hydroxypropyl cellulose (7) was characterized by SAXS. As reported in Figure 6, the SAXS curve of the cellulose ether showed a low Q typical of a linear polymer chain in a dilute solution. This curve was fitted with the well-known Debye form factor:

$$I(Q) = K \times 2(e^{-x} + x - 1)/x_2 + \text{bkg} \quad (5)$$

where $x = (QR_g)^2$, I = SAXS Intensity, K is the normalization factor, R_g is the radius of gyration, and bkg is the constant background term. The extracted values were $K = 7.3 \pm 1.9$ (arbitrary units), $R_g = 313 \pm 47$ Å, and $\text{bkg} = 0.036 \pm 0.003$ (arbitrary units).

The average R_g associated with the sample was about 31 ± 5 nm. Because of the limited accessible Q range, this value represented a low-limit estimation of the real characteristic dimension. These data, referring to the cellulose ether molecular weights, were in agreement with the dispersion of solvent-swollen macromolecular aggregates.

Treatment of the lignin flours with cellulose ethers

To evaluate the ability of the cellulose ethers synthesized to penetrate inside the waterlogged wood, preliminary tests on recent oak wood lignin samples were performed. The choice of powdered lignin as the material for these treatments permitted us to evaluate the affinity of the consolidants for partially or strongly degraded samples in which the cellulosic component was partially lost in a such way that residue wood was mainly formed by lignin.

Lignin samples were prepared from wood flours by standard procedures,²⁵ then maintained for 24 h in aqueous colloidal dispersions of the consolidants, and magnetically stirred at room temperature. After filtration, washing, and drying at 60°C (in this step,

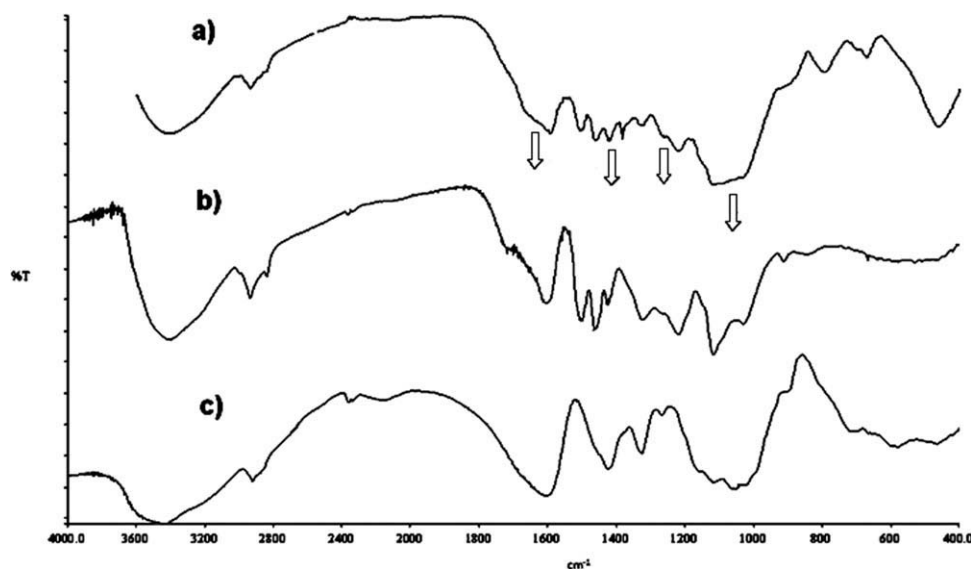


Figure 7 FTIR spectra of (a) oak wood lignin treated with CMC, (b) oak wood lignin, and (c) CMC.

the allylated cellulose ethers were subjected to cross-linking), the samples were analyzed through FTIR spectroscopy; then, the spectra were compared with those of the untreated lignin and the cellulose ethers to evaluate the effectiveness of the treatment.

Infrared spectra of wood flours allowed us to characterize the degradation state of wood manufacturing products and evaluate the ratio between the cellulose and lignin peaks. In detail, for oak wood lignin [Fig. 7(b) and Table III], the peaks at 1219 and 1116 cm^{-1} were characteristic of syringyl,²⁶ those at 1603 and 1501 cm^{-1} were related to aromatic ring stretching,²⁷ and the one at 1464 cm^{-1} was related to CH bending.²⁷

Three cellulose ethers were tested on the lignin samples: two synthesized products, lower DP allyl carboxymethyl cellulose (3) and lower DP allyl *n*-hydroxypropyl cellulose (7), were compared with commercial CMC.

From the analysis of the FTIR spectrum of lignin treated with CMC (Fig. 7, Table III), it was possible to confirm the absorption of the product by observation of the variation in the shape of the lignin characteristic peak (1603 cm^{-1}) due to the overlapping of a peak at 1611 cm^{-1} related to the COO^- stretching of CMC. We also observed variations in the relative

intensities of peaks at 1460, 1418, 1381, and 1325 cm^{-1} ; an increase in the peak at 1029 cm^{-1} ; and a new peak at 1058 cm^{-1} due to the C—O stretching of CMC.

From the analysis of the FTIR spectrum of the lignin treated with lower DP allyl carboxymethyl cellulose (3; Fig. 8 and Table III), it was possible to confirm the absorption of the product by observation of the increase in the intensity of the peak at 1609 cm^{-1} due to the overlapping of the peak at 1614 cm^{-1} related to the COO^- stretching of the cellulose ether with the lignin peak. The increase in the peaks at 1418 and 1029 cm^{-1} and the presence of a new peak at 1062 cm^{-1} (C—O stretching of the consolidant) confirmed the absorption of the product.

The FTIR spectrum of the lignin treated with lower DP allyl *n*-hydroxypropyl cellulose (7; Fig. 9 and Table III) showed a strong decrease in the peak at 1502 cm^{-1} with respect to other absorption peaks and a variation in the intensities of the peaks at 1465 and 1423 cm^{-1} due to the overlapping of the peak at 1448 cm^{-1} related to the consolidant. Moreover, we observed a new peak at 1372 cm^{-1} and a variation in the range between 1161 and 1034 cm^{-1} , in which more intense peaks of the product could be found, in particular, peaks at 1060 and 1035 cm^{-1} .

TABLE III
Summary of the Relevant FTIR Transitions (cm^{-1})

	Syringyl	Aliphatic C—H bending	Aromatic ring C—C stretching	COO^- stretching	C—O stretching	O—H bending
Lignin	1119 and 1216	1464	1501 and 1603			
Carboxymethyl cellulose		1418		1611	1058	
Allyl carboxymethyl cellulose		1418		1614	1062	
Allyl <i>n</i> -hydroxypropyl cellulose		1448			1035 and 1060	1372

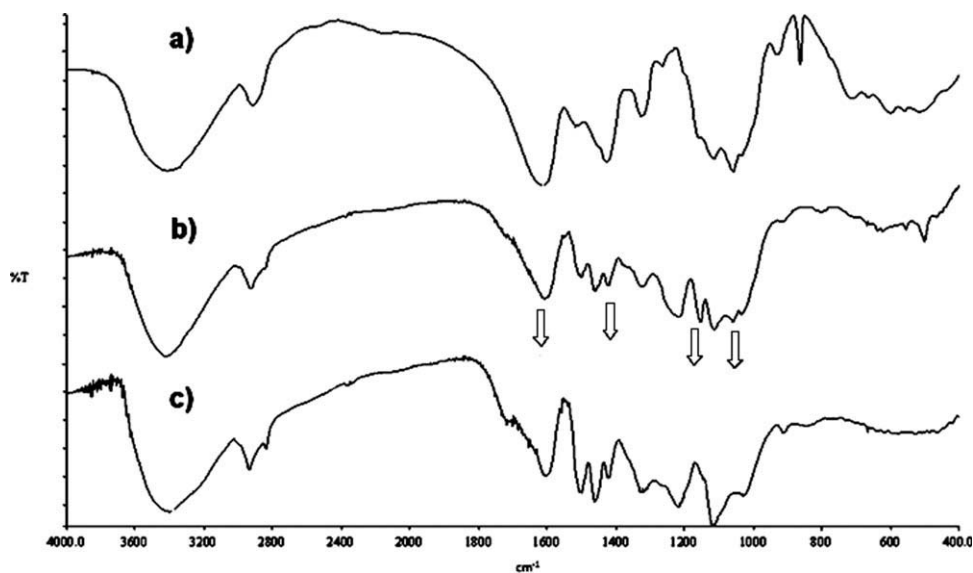


Figure 8 FTIR spectra of (a) lower DP allyl carboxymethyl cellulose (3), (b) oak wood lignin treated with lower DP allyl carboxymethyl cellulose (3), and (c) oak wood lignin.

Reversibility of the consolidating treatments

A complete reversibility of the treatment could lead to excessive mobility of the consolidant inside a wood structure. This could damage wood manufacturing products, so it is preferable to have incomplete reversibility of the treatment. Reversibility is then an indispensable feature for superficial treatments, in which product alteration can modify the aesthetic appearance of an artwork or of an archeological find-

ing, whereas in consolidating treatments, the mechanical and physical resistance prevail over other factors. For this reason, it is really important to achieve a low mobility of the consolidant inside wood.

To evaluate the reversibility and mobility of the cellulose ethers applied on wood, lignin samples treated with the consolidants were then added to demineralized water and magnetically stirred for 24 h at room temperature. After centrifugation and drying at 60°C, the samples were analyzed again

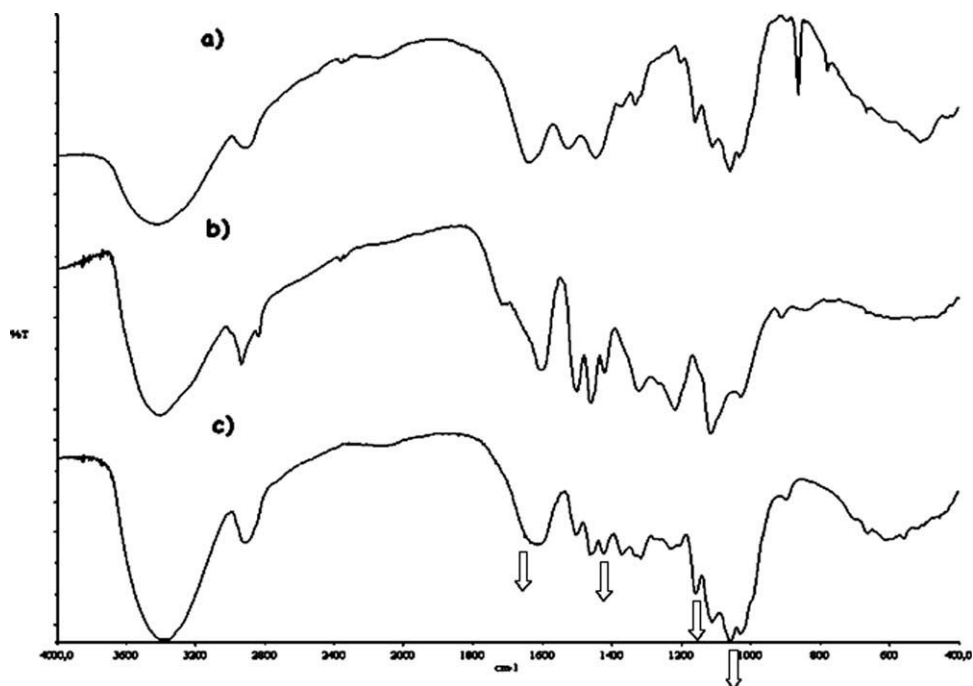


Figure 9 FTIR spectra of (a) lower DP allyl *n*-hydroxypropyl cellulose (7), (b) oak wood lignin, and (c) oak wood lignin treated with lower DP allyl *n*-hydroxypropyl cellulose (7).

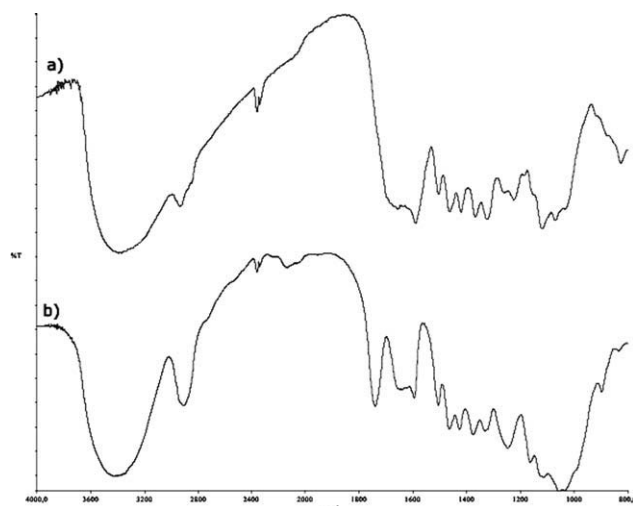


Figure 10 FTIR spectra of (a) degraded oak wood and (b) recent oak wood.

through FTIR spectroscopy, and the spectra were compared with those related to the treated lignin samples.

From the analysis of the FTIR spectrum of the lignin treated with CMC and followed by a wash, we observed that the product was almost completely removed. In fact, there was an increase in the peak at 1463 cm^{-1} , characteristic of lignin; a decrease in the one at 1422 cm^{-1} ; and the disappearance of the one at 1381 cm^{-1} . However, the intensity of the peak at 1029 cm^{-1} compared to the one at 1122 cm^{-1} related to lignin confirmed a slight presence of the consolidant even after washing.

From the analysis of the FTIR spectrum of the lignin sample treated with lower DP allyl carboxymethyl cellulose (3) and washed, we observed how the consolidant was only partially removed, as shown by the slight decreases in the intensity of peaks at 1617 , 1504 , 1320 , 1215 , and 1113 cm^{-1} .

From the analysis of the FTIR spectrum of the lignin sample treated with lower DP allyl *n*-hydroxypropyl cellulose (7) and washed, we observed that only a small fraction of consolidant was removed, and this was demonstrated by the increase in the intensity of the peaks at 1502 and 1420 cm^{-1} , characteristic of lignin; the consequent decrease in the one at 1456 cm^{-1} ; and the disappearance of the peak at 1372 cm^{-1} . Moreover, a change in the shape of the peak at 1227 cm^{-1} was evident, and this was due to the disappearance of the peak at 1205 cm^{-1} , characteristic of the consolidant. To verify whether a longer water treatment could remove the consolidant completely, a second washing treatment was performed on this lignin sample. The intensities of the consolidant's characteristic peaks decreased only slightly, and the presence of the consolidant's peaks at 1060 and 1029 cm^{-1} and the comparison with the spectrum of the

initial lignin sample confirmed a high retention of this cellulose ether even after the second washing. This behavior was in agreement with the reactivity of the allylic groups, which underwent a crosslinking reaction once the sample was subjected to heating. From the analysis of the FTIR spectra, it was not possible to prove the formation of covalent bonds between the different chains of the cellulose ether or between these and lignin. To confirm the crosslinking behavior of the allylated cellulose ethers, samples of each consolidant were heated at 60°C for 6 h and then added to demineralized water. The loss of solubility in water of the compounds after the heating process were taken as a proof of the crosslinking. The same reactivity was observed when the consolidants absorbed in the lignin flours were heated at 60°C during the drying procedure.

Treatment of the degraded wood with a cellulose ether

A further test of wood penetration was performed on a degraded oak wood cubic sample obtained from an archaeological find. The prevailing presence of lignin versus cellulose in this wooden block was evaluated by comparison of the FTIR spectrum of its pre-extracted flours with the one of recent oak wood flours (Fig. 10).

The sample was kept in a colloidal dispersion of lower DP allyl carboxymethyl cellulose (3) for 20 days at room temperature. After washing and drying at 60°C , the weight of the sample increased. A fragment of the sample was recovered from the internal section and analyzed through FTIR spectroscopy; then, the spectrum was compared with that of the untreated wood sample. From the analysis of these FTIR spectra, we observed only a slight variation in the shape of the peaks in the range 1000 – 1100 cm^{-1} ; this was in agreement with the absorption of the consolidant in the recovered section of the sample. However, even the lower DP cellulose ether synthesized was too bulky to penetrate efficiently. In addition, the low amount of the consolidant penetrated in the wood sample could have been related to the short time of the treatment and to the presence of macromolecular aggregates.

CONCLUSIONS

In this study, some novel polysaccharide compounds derived from cellulose were synthesized and characterized, and the possibility of using these compounds as consolidants for waterlogged wood was evaluated. In detail, some crosslinkable cellulose ethers were chosen for this purpose. The choice of this kind of polymer was made after an accurate study of the degradation process of waterlogged

wood manufacturing products. In fact, the cellulosic and hemicellulosic components of wood are the most involved in these processes because of their higher sensitivity to hydrolysis reactions. The synthesized ethers were then used for a preliminary application on lignin flour samples to evaluate, through FTIR spectroscopy, the absorption of the polymers for degraded wood: the cellulose ethers showed a very high affinity for lignin, which is the main component in strongly degraded wood samples. In addition, the reversibility of these treatments was evaluated; the polymers showed a high retention in the lignin samples, and this was due to the crosslinking reactions of the allyl ethers that we used. This led to an insoluble network and then to a very low reversibility of this kind of polymer in the treatment of the waterlogged wood. In contrast, in the treatment of lignin with commercial sodium carboxymethyl cellulose, a high reversibility was noticed, and the amount of consolidant removed was high. The absence of reversibility for allyl derivatives was in agreement with a crosslinking reaction. A test of wood penetration, performed on a degraded wood cubic sample with lower DP allyl carboxymethyl cellulose (3), showed penetration of the consolidant, as observed from the FTIR and gravimetry studies. However, the low weight increase of the wood sample could be attributed to several factors, such as the molecular weight of the consolidant, the presence of macromolecular aggregates in the colloidal dispersion, and finally, the treatment time used in the penetration test, which was lower than the ones usually used for wood consolidation.²⁸

From these studies, it seems possible that these polysaccharide compounds could be used as wood consolidating agents. However, more information is required to evaluate how the presence of these compounds changes wood's physical features. With this purpose, an analytical protocol should be used to gain parameters required to improve the chemical structures of new compounds useful for wood conservation. Future study is required to analyze the ability of cellulose derivatives to consolidate wooden artwork.

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