Synthesis of Hydroxylated Oligoamides for Their Use in Wood Conservation

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ABSTRACT: Some oligo- or polyamides containing several hydroxyl groups were synthesized in order to obtain new water-soluble compounds with a high affinity for polar materials as wood, paper, and natural fibers. The interest for the synthetic procedures is the use of renewable sources as starting compounds. In fact natural compounds or their derivatives, as L-tartaric acid, D(+)-glucaric acid and α,α-trehaluronic acid, were used as dicarboxylic acids in the polycondensation reactions, in order to obtain several functionalized oligoamides. All the compounds obtained in this study were characterized through FTIR and NMR spectroscopy. The oligoamides, water-soluble and not provided with high-molecular weights, were tested as wood consolidants. Physical properties like hygroscopicity of stabilized wood, volume shrinkage, density, and basic density were evaluated on the treated samples and compared with those obtained in the same conditions for an untreated archeological sample and a recent wood sample. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

In the past, several compounds and methods have been studied and used for the treatment of waterlogged wood.[1–3] Polyethylene glycols (PEGs) at different molecular weights are still today the most used compounds for wood consolidation.[4,5] In fact in the wood lifetime various agents can alter the chemical structure of its main components. In particular, water and biological agents can favor hydrolysis reactions which cause the prevalent loss of hemicelluloses and cellulose, which represent the backbone of the wood structure. However, in the last years, several problems for the wooden manufactured products have emerged due to the presence of PEG or other synthetic consolidants.[6]

To respect the natural characteristics of wood, a better solution in the field of conservation could be to avoid the use of a consolidant. However this decision requires a good condition of the wooden find and a particular technique to remove the water. Generally, degraded wooden manufactured products require the presence of a consolidant and in this case it is important to select a product which respects chemical, physical and mechanical properties of wood.

The aim of this study is the synthesis and characterization of some novel compounds provided with a chemical structure similar to the wood or characterized by a structural affinity for the main wood components, in order to obtain a structure consolidation without producing an alteration of the physical characteristics.

In agreement with this purpose, at the beginning of this research, several synthetic cellulose derivatives have been studied as consolidants provided with a chemical structure similar to that of cellulose and hemicelluloses which are generally the main degraded components in the wooden structure. Different types of water-soluble polysaccharides have been obtained from cellulose etherification reactions and preliminary tests of application of these products on archaeological wood samples have been performed.[7] Despite a good interaction capability of the synthesized compounds with wood components, a poor penetration ability has been observed due to their high molecular weights, even using hydrolyzed cellulose as starting material.

Now we report the syntheses and characterization of several hydroxylated oligoamides in order to obtain water-soluble

compounds with a high affinity for polar materials and lower molecular weights with respect to the cellulose derivatives. The interest for the synthetic pathways is the use of renewable resources as starting compounds. In fact natural compounds or their derivatives, as L-tartaric acid, D(+)-glucaric acid and α,α-trehaluronic acid, have been used as hydroxylated diacids in the polycondensation reactions. The syntheses of different hydroxylated nylons are reported in the literature.[8–11] Generally these hydroxylated polyamides have been obtained as condensation products from activated carbohydrate diacids (aldaric acids) and diamines. In particular Minoura et al. first reported the polycondensation of D-tartaric acid with some diamines,[12] while Ogata et al. reported the syntheses of poly(hexamethylene L-tartaramide)[13,14] and poly(hexamethylene galactaramide)[15] by condensation of hexamethylenediamine with dimethyl L-tartrate and diethyl galactarate, respectively, in polar solvents.

Subsequently Kiely et al. described simple procedures, that do not require carbohydrate hydroxyl protection/deprotection steps, in order to obtain D(+)-glucaric acid-based polymers, starting with inexpensive and commercially available D(+)-glucose.[16–18]

In this work, using modified versions of the procedures reported in the literature, the polycondensation reactions between different dimethyl esters and an aliphatic diamine were performed in order to obtain oligoamides with different behavior. In fact products with different molecular weight and different hydrophilic/hydrofobic ratio were obtained using 1,2-ethylenediamine and dimethyl esters obtained from L-tartaric acid, D(+)-glucaric acid, and α, α-trehaluronic acid.

Preliminary tests of application of the synthesized polymers on archaeological wood samples were then performed in order to verify their ability to penetrate inside a wooden structure. A specific diagnostic protocol[19] was used in order to highlight some positive and negative features of the new products studied as consolidants. In fact, in order to design new consolidants for wood impregnation and to select the consolidant with the best performance, a rapid screening of the synthesized products is required in order to modify the structure of the consolidant. With this goal, small wooden samples were used for these tests, with a treatment time lower than the one used in the standard conservation procedures. After the treatment, the chemical affinity for wood and some physical wood properties like hygroscopicity, volume shrinkage, density, and basic density were evaluated.

EXPERIMENTAL

Materials

L-tartaric acid, boric acid, (diacetoxyiodo)benzene (BAIB), Amberlite IR-120H, ethylenediamine, sodium nitrite, 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), 1,4-dioxane, 2-propanol were purchased from Aldrich. Acetyl chloride, potassium hydroxide, triethylamine were purchased from Carlo Erba. α,α-Trehalose, ethanol were purchased from Fluka. Methanol was purchased from Normapur. Hydrogen chloride, nitric acid, D(+)-glucose were purchased from Riedel-De Haën. Deuterated solvents (CDCl₃, D₂O) were purchased from Aldrich. Amberlite IR-120H resin was activated by washing with methanol (3 × 10

mL) and left overnight in methanol (10 mL). All chemicals are reagent grade and were used without further purification.

Instruments

^{1}H-NMR, ^{13}C-NMR spectra were recorded with a Varian Mercury Plus 400 spectrometer and on a Varian VXR 200 spectrometer, working at 399.921 MHz and 199.985 MHz, respectively. All spectra are reported in ppm and referred to TMS as internal standard. Spectra elaboration was subsequently executed with software Mestre-C 4.3.2.0.

FTIR spectra were recorded with a Perkin-Elmer Spectrum BX model, and elaborated with software Spectrum v. 3.02.02. The solutions were analyzed using KBr or CaF₂ round cell windows, after deposition and evaporation of solvent. Spectra of solid samples were recorded as KBr pellets.

Mass spectra were recorded with a Bruker Daltonic Ultraflex MALDI TOF/TOF spectrometer. Glass transition temperatures (T_g) were detected by Differential Scanning Calorimetry (DSC), with a TA instruments DSC Q2000 calorimeter, working with a temperature gradient of 5°C/min, starting from room temperature. Data elaboration was subsequently executed with software Universal Analysis 2000.

Synthesis of the Consolidants. Dimethyl L-tartrate,[20] potassium hydrogen D(+)-glucarate,[21] dimethyl D(+)-glucarate[22] were synthesized using modified versions of the synthetic procedures reported in the literature.

α,α-Trehaluronic Acid. Into a dry 100-mL flask, TEMPO (305 mg, 1.95 mmol) was added under continuous stirring to 45 mL of a 1,4-dioxane/water (2:1) solution of α,α-trehalose (1.5 g, 4.4 mmol). BAIB (7.0 g, 21.9 mmol) was then added, and the mixture was allowed to react at room temperature. The reaction, monitored by thin layer chromatography (2-propanol/water, 3:1), was completed in 16 h. After vacuum distillation at 60°C, a yellow solid was obtained (1.6 g, 97.4% yield). ^{1}H-NMR (D₂O, 400 MHz): 3.62 ppm (dd, $J_{4,5}$ 10.0 Hz, $J_{4,3}$ 9.2 Hz, 2H, H_4, $H_{4'}$); 3.72 ppm (dd, $J_{2,3}$ 9.6 Hz, $J_{2,1}$ 3.6 Hz, 2H, H_2, $H_{2'}$); 3.88 ppm (m, 2H, H_3, $H_{3'}$); 4.36 ppm (d, J 10.0 Hz, 2H, H_5, $H_{5'}$); 5.23 ppm (d, J 3.6 Hz, 2H, H_1, $H_{1'}$). ^{13}C-NMR (D₂O, 100 MHz): 70.4 ppm (C_4, $C_{4'}$); 71.1 ppm (C_5, $C_{5'}$); 71.4 ppm (C_3, $C_{3'}$); 72.0 ppm (C_2, $C_{2'}$); 94.2–94.3 ppm (C_1, $C_{1'}$); 173.2 ppm (-$\underline{C}$OOH).

Dimethyl-α,α-trehaluronate. Into a 40-mL Sovirel® tube, Amberlite IR-120H (3.5 g) was added to 25 mL of a methanol solution of α,α-trehaluronic acid (1.71 g, 4.62 mmol), and the mixture was heated at 80°C under gentle stirring. The reaction, monitored by thin layer chromatography (2-propanol/water, 3:1), was completed in 48 h. The mixture was cooled to room temperature and filtered, then the solution was distilled under reduced pressure at 50°C. The orange solid obtained was dried in vacuum at room temperature (1.67 g, 91.0% yield). ^{1}H-NMR (D₂O, 400 MHz): 3.64 ppm (dd, $J_{4,5}$ 10.0 Hz, $J_{4,3}$ 9.2 Hz, 2H, H_4, $H_{4'}$); 3.73 ppm (dd, $J_{2,3}$ 9.6 Hz, $J_{2,1}$ 3.6 Hz, 2H, H_2, $H_{2'}$); 3.85 ppm (s, 6H, -COOCH_3); 3.88 ppm (m, 2H, H_3, $H_{3'}$); 4.44 ppm (d, J 10.0 Hz, 2H, H_5, $H_{5'}$); 5.22 ppm (d, J 3.6 Hz, 2H, H_1, $H_{1'}$). ^{13}C-NMR (D₂O, 50 MHz): 53.1 ppm (-COO$\underline{C}$H₃);

70.4 ppm (C_4, $C_{4'}$); 71.2–71.4 ppm (C_5, $C_{5'}$; C_3, $C_{3'}$); 72.0 ppm (C_2, $C_{2'}$); 94.4 ppm (C_1, $C_{1'}$); 171.3 ppm (-$\underline{C}$OOH).

Polyethylene-L-tartaramide. Into a 40-mL Sovirel® tube, triethylamine (0.21 mL, 1.5 mmol) was added under continuous stirring to 25 mL of a methanol solution of dimethyl L-tartrate (0.99 g, 5.55 mmol). Ethylenediamine (0.37 mL, 5.55 mmol) was added and the mixture was heated at 80°C for 7 days. After cooling to room temperature, the mixture was filtered on a Büchner funnel and the solid obtained was dried at 75°C (892 mg, 67.4% yield). ^{1}H-NMR (D_2O, 400 MHz): 3.47 ppm (m, 4H, -CH_2NH-); 4.58 ppm (m, 2H, -CHOH). ^{13}C-NMR (D_2O, 100 MHz): 38.5 ppm (-$\underline{C}H_2$NH-); 72.3 ppm (-$\underline{C}$HOH); 174.0 ppm (-$\underline{C}$ONH). FTIR (KBr pellets): peaks at 3338 (vs, broad, O—H stretching), 2936 (w, C—H stretching), 2879 (s, C—H stretching), 1654 (vs, stretching C=O amide), 1541 (s, bending N—H amide), 1437 (w C—H bending), 1134 (w, stretching C—O), and 1072 (w, stretching C—O) cm^{-1}. $T_g = 103.9$°C.

Polyethylene-D(+)-glucaramide. A modified version of the synthetic procedure reported by Kiely et al.[22] was used.

Into a 25-mL Sovirel® tube, triethylamine (0.63 mL, 4.52 mmol) was added under continuous stirring to 10 mL of a methanol solution of dimethyl D(+)-glucarate (0.8 g, 3.36 mmol). Ethylenediamine (0.22 mL, 3.36 mmol) was added and the mixture was allowed to react at room temperature for 5 days. After cooling to room temperature, the mixture was filtered on a Büchner funnel and the solid obtained was dried at 70°C (565 mg, 56.4% yield). ^{1}H-NMR (D_2O, 400 MHz): 3.45 ppm (m, 4H, -CH_2NH-); 3.98 ppm (m, 1H, H_3); 4.12 ppm (m, 1H, H_2); 4.27 ppm (m, 1H, H_4); 4.35 ppm (m, 1H, H_1). ^{13}C-NMR (D_2O, 100 MHz): 38.4 ppm (-$\underline{C}H_2$NH-); 71.0-73.6 ppm (C_1, C_2, C_3, C_4); 178.2-178.5 ppm (-$\underline{C}$ONH). FTIR (KBr pellets): peaks at 3312 (vs, broad, O—H stretching), 2939 (w, C—H stretching), 2870 (w, C—H stretching), 1644 (vs, stretching C=O amide), 1537 (s, bending N—H amide), 1435 (w C—H bending), 1127 (m, stretching C—O), 1084 (m, stretching C—O) and 1060 (m, stretching C—O) cm^{-1}. $T_g = 77.2$°C.

Polyethylene-α,α-trehaluronamide. Into a 40-mL Sovirel® tube, triethylamine (0.14 mL, 1.0 mmol) was added under continuous stirring to 25 mL of a methanol solution of dimethyl-α,α-trehaluronate (1.44 g, 3.62 mmol). Ethylenediamine (0.24 mL, 3.62 mmol) was added and the mixture was allowed to react at room temperature for 4 days. After cooling to room temperature, the mixture was filtered on a on a Büchner funnel and the brown solid obtained was washed with methanol and dried at 70°C (629 mg). The filtrated solution was heated at 80°C under continuous stirring for 7 days. After cooling to room temperature, the mixture was filtered on a on a Büchner funnel and the brown solid obtained was washed with methanol and dried at 70°C (161 mg). The two products were collected (790 mg, 47.6% yield). ^{1}H-NMR (D_2O, 400 MHz): 3.58 ppm (m, 4H, -CH_2NH-); 3.64 ppm (m, 2H, H_4, $H_{4'}$); 3.73 ppm (m, 2H, H_2, $H_{2'}$); 3.88 ppm (m, 4H, H_3, $H_{3'}$); 4.28 ppm (m, 2H, H_5 $H_{5'}$); 5.23 ppm (m, 2H, H_1, $H_{1'}$). ^{13}C-NMR (D_2O, 100 MHz): 38.9 ppm (-$\underline{C}H_2$NH-); 70.4 ppm (C_4, $C_{4'}$); 70.7 ppm (C_5, $C_{5'}$); 71.6 ppm (C_3, $C_{3'}$); 72.0 ppm (C_2, $C_{2'}$); 93.8 ppm (C_1, $C_{1'}$); 176.3 ppm (-$\underline{C}$ONH). $T_g = 133.1$°C. FTIR (KBr pellets): peaks at

peaks at 3381 (vs, broad, O—H stretching), 2931 (w, C—H stretching), 1738 (w, stretching C=O ester), 1661 (vs, stretching C=O amide), 1550 (s, bending N—H amide), 1104 (m, stretching C—O), 1067 (m, stretching C—O) and 1028 (m, stretching C—O) cm^{-1}.

Wood Flours Preparation and Soxhlet Extraction. Beech wood sample flour was obtained 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. FT-IR (KBr pellets): peaks at 3381 (vs, broad, O—H stretching), 2931 (w, C—H stretching), 1606 (vs, aromatic C=C), 1509 (s, aromatic C=C), 1460 (s, C—H bending), 1423 (s, aromatic C=C), 1314 (s, stretching C—O), 1219 (vs, stretching C—O) and 1115 (s, stretching C—O) cm^{-1}.

Lignin Treatments

Treatment of Lignin with Polyethylene-L-tartaramide. Into a dry 25-mL flask, beech lignin (15 mg) was added to a solution of polyethylene-L-tartaramide (150 mg) in demineralized water (10 mL) and maintained under continuous stirring for 24 h at room temperature. The mixture was centrifuged, and the solid residue was dried at 60°C for 24 h.

FTIR (KBr pellets): peaks at 3381 (vs, broad, O—H stretching), 2931 (w, C—H stretching), 1738 (w, stretching C=O ester), 1661 (vs, stretching C=O amide), 1550 (s, bending N—H amide), 1104 (m, stretching C—O), and 1067 (m, stretching C—O).

Treatment of Lignin with Polyethylene-D(+)-glucaramide. Into a dry 25-mL flask, beech lignin (15 mg) was added to a solution of polyethylene-D(+)-glucaramide (150 mg) in demineralized water (10 mL) and maintained under continuous stirring for 24 h at room temperature. The mixture was centrifuged, and the solid residue was dried at 60°C for 4 days.

FTIR (KBr pellets): peaks at 3320 (vs, broad, O—H stretching), 2939 (w, C—H stretching), 2870 (w, C—H stretching), 1644 (vs, stretching C=O amide), 1537 (s, bending N—H amide), 1435 (w, C—H bending) and 1118 (m, broad, stretching C—O) cm^{-1}.

Treatment of Lignin with Polyethylene-α,α-trehaluronamide. Into a dry 25-mL flask, beech lignin (15 mg) was added to a solution of polyethylene-α,α-trehaluronamide (150 mg) in demineralized water (10 mL) and maintained under continuous stirring for 24 h at room temperature. The mixture was centrifuged, and the solid residue was dried at 60°C for 4 days.

FTIR (KBr pellets): peaks at 3381 (ff, broad, O—H stretching), 2931 (d, C—H stretching), 1661 (ff, stretching C═O amide), 1550 (f, bending N—H amide) and 1113 (f, broad, stretching C—O) cm^{-1}.

Degraded Wood Treatments
Specimens Preparation. The oak wood specimens were recovered from an archaeological waterlogged find located in Poggiomarino, Italy. Three cubic specimens were prepared and mass and volume were measured at maximum water content (MWC):

- Specimen "A": $M = 1.56$ g; $V = 1.40$ cm^3
- Specimen "B": $M = 2.52$ g; $V = 2.25$ cm^3
- Specimen "C": $M = 1.61$ g; $V = 1.47$ cm^3

The specimens were immersed in demineralized water and kept at room temperature in these conditions until the beginning of the treatment.

Treatment of Specimen "A" with Polyethylene-L-tartaramide. Into a 25-mL Sovirel® tube, the specimen "A" was immersed in 8.5 mL of a water solution of polyethylene-L-tartaramide (382 mg) and kept at room temperature in these conditions for 57 days.

Treatment of Specimen "B" with Polyethylene-D(+)-glucaramide. Into a 25-mL Sovirel® tube, the specimen "B" was immersed in 7.0 mL of a water solution of polyethylene-D(+)-glucaramide (500 mg) and kept at room temperature in these conditions for 57 days.

Treatment of Specimen "C" with Polyethylene-α,α-trehaluronamide. Into a 25-mL Sovirel® tube, the specimen "C" was immersed in 7.0 mL of a water solution of polyethylene-α,α-trehaluronamide (500 mg) and kept at room temperature in these conditions for 57 days.

Physical Characterization. A protocol similar to the international technical standards UNI ISO 3131 normative[23] was used for the physical characterization. The weights of the specimens treated with the different consolidants at relative humidities (R.H.) of 100, 86, 65, and 10% were evaluated. For this work, in order to evaluate the basic density, the final temperature was 50°C (R.H. 12%), different from the one reported by the normative UNI ISO 3131 (103°C), corresponding with the anhydrous state (R.H. 0%).

Each wood specimen was measured for volume at maximum water content (MWC) using the water displacement method.

RESULTS AND DISCUSSION
Synthesis and Characterization of Hydroxylated Polyamides
The procedures used for the synthesis of the monomers and of the polyamides were specific in order to obtain products with the structural characteristics required for their use as wood consolidants. In fact polymers with too high molecular weights or unwanted degradation products could be obtained from hydroxylated monomers by heating their salts as reported for the industrial synthesis of common nylons.

The first polyamide synthesized in this work was the polyethylene-L-tartaramide. The two monomers used for the synthesis were L-tartaric acid and ethylenediamine. L-tartaric acid was
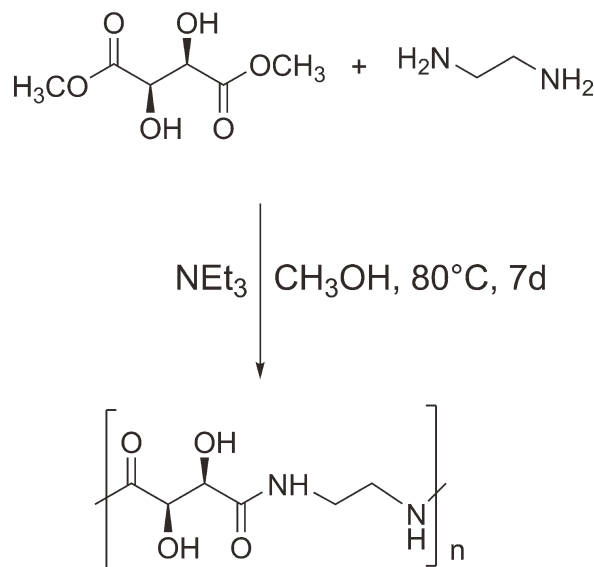

Figure 1. Synthesis of polyethylene-L-tartaramide.

chosen because of the presence of two hydroxyl groups in the molecule, and this feature makes its structure similar to the one of a carbohydrate in its open-chain form. Ethylenediamine was chosen because it was the simplest and the most available commercial diamine. To carry out the polycondensation reaction, it was required to "activate" the dicarboxylic monomer to promote the condensation with the diamine. Among the existing methods used to activate the acid, the synthesis of the dimethyl ester was chosen because it is usually a quite simple reaction. In addition, it avoids the use of expensive reagents and a few byproducts are formed during the reaction. The synthesis of dimethyl L-tartrate was carried out following the procedure reported by Houston et al.,[20] but using a higher reaction temperature (80°C).

For the polycondensation reaction between dimethyl L-tartrate and ethylenediamine, several attempts were made by varying the reaction parameters (time, temperature, solvent, catalyst). The best conditions for the synthesis were found using methanol as a solvent and triethylamine as a catalyst and heating at 80°C for 7 days (Figure 1). The product was soluble in cold water.

The degree of polymerization (DP) calculated by mass spectrometry MALDI-MS was between 3 and 11, with an average value of 4 ($M_n = 700$ g/mol). The glass transition temperature (T_g), evaluated by differential scanning calorimetry (DSC) using a temperature gradient of 5°C/min starting from room temperature, was 103.9°C.

To expand the possibilities of application on waterlogged wood and to obtain more than one macromolecular compound with the desired properties, a second polyamide, reported in literature by Kiely et al.,[22] was selected and synthesized. In this case, the dicarboxylic monomer used was D(+)-glucaric acid, while the diamine monomer used was ethylenediamine. D(+)-Glucaric acid is a derivative of D(+)-glucose, and for this reason it has many advantages: first of all, four hydroxyl groups are present in the molecule, and this will enhance the hydrophilicity of the
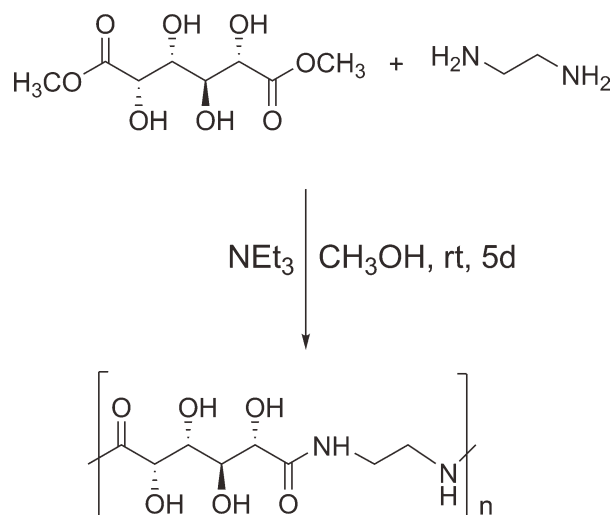
Figure 2. Synthesis of polyethylene-D(+)-glucaramide.

polyamide, resulting in an improvement of the affinity for wood's components. In addition, the high availability and the low cost of the precursor, together with the facility to obtain this derivative, make the process quite favorable. Finally, the use of natural compounds as precursors makes the polyamide synthesis a fully biocompatible process.

D(+)-Glucaric acid was obtained[21] through the strong oxidation of D(+)-glucose, isolated as the monopotassium salt, and converted in the dimethyl D(+)-glucarate.[22] The subsequent polycondensation reaction with ethylenediamine was carried out by using the same conditions of the previous polymerizations, but maintaining the mixture at room temperature for 5 days[22] (Figure 2). The product was soluble in cold water.

The degree of polymerization (DP) calculated by mass spectrometry MALDI-MS was between 2 and 8, with an average value of 3 ($M_n = 705$ g/mol). The glass transition temperature (T_g), evaluated by differential scanning calorimetry (DSC) using a temperature gradient of 5°C/min starting from room temperature, was 77.2°C.

The third polyamide synthesized in this work was polyethylene-α,α-trehaluronamide, obtained using α,α-trehaluronic acid as the dicarboxylic acid and ethylenediamine as the diamine. α,α-Trehaluronic acid is a synthetic derivative of α,α-trehalose, a disaccharide constituted by two units of D(+)-glucose joined together through a α-1,1-glycosidic bond. α,α-Trehalose is a natural disaccharide largely available and it has many interesting features. However, though these features are well known since many years, this compound has never been produced on an industrial scale. Recently, some innovative enzymatic systems able to obtain α,α-trehalose on a large scale have been developed,[24] and this allowed to greatly reduce its price and to increase the number of applications where it can be used. From a chemical point of view, since the two D(+)-glucose molecules are joined together by their anomeric positions, α,α-threhalose does not show any reducing power. For this reason, this disaccharide is one of the most stable carbohydrates, having a good thermal stability and an excellent chemical resistance in a large

pH range. In addition, since it hasn't got any free anomeric positions, it does not undergo to the Maillard reaction with aminic compounds like amino acids or proteins. For these reasons, trehalose is an extremely attractive compound for many industrial applications. For our purpose, the use of a trehalose derivative as a monomer allowed to introduce in the polyamide backbone a "carbohydrate-derived" molecule, being this one of the main objectives requested in this work. In addition, there was the advantage of using a natural compound, biocompatible, and biodegradable, with a good stability and a relatively low cost.

α,α-Trehaluronic acid was synthesized from α,α-trehalose through a selective oxidation of the two primary hydroxyl groups on the C_6 and C_6', using the TEMPO/BAIB oxidation system (Figure 3).

Also in this case, the acid precursor was activated by the synthesis of the dimethyl ester, using Amberlite IR-120H ion-exchange resin as the catalyst and heating the mixture at 80°C (Figure 4).

The polycondensation of dimethyl α,α-trehaluronate with ethylenediamine was carried out by using the same conditions of the previous polymerizations, but working at room temperature for 4 days and then at 80°C for 7 days. Polyethylene-α,α-trehaluronamide, isolated by filtration (Figure 5), was soluble in cold water.

The degree of polymerization (DP) calculated by mass spectrometry MALDI-MS was between 1 and 5, with an average
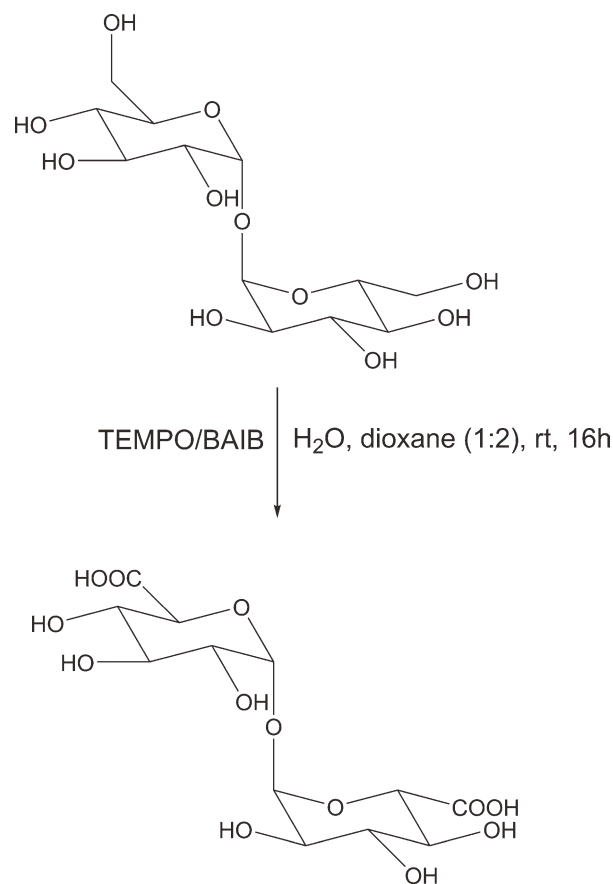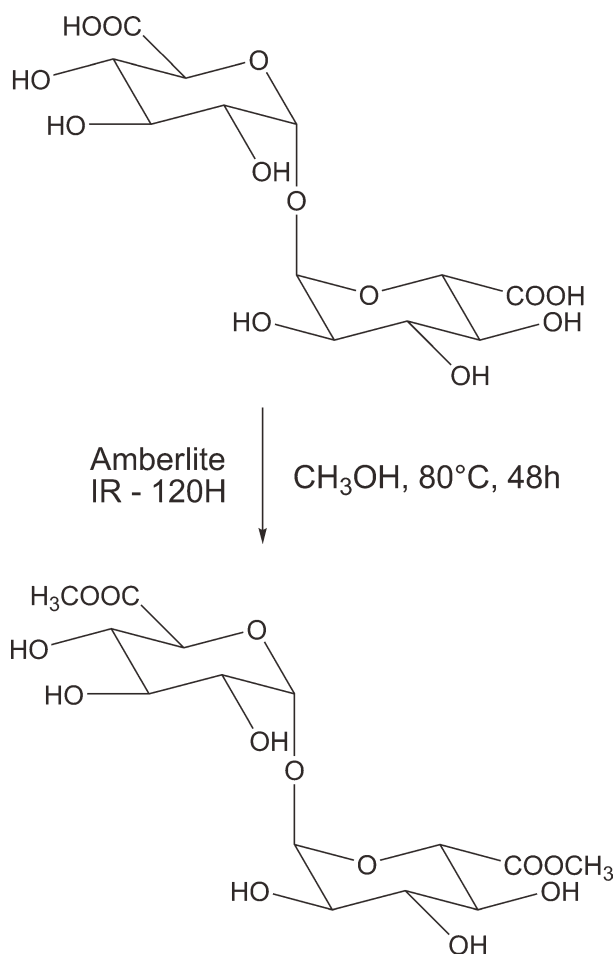

Figure 3. Synthesis of α, α-trehaluronic acid.

Figure 4. Synthesis of dimethyl-α, α-trehaluronate.

value of 2 ($M_n = 790$ g/mol). The glass transition temperature (T_g), evaluated by differential scanning calorimetry (DSC) using a temperature gradient of 5°C/min starting from room temperature, was 133.1°C.

Treatment of the Lignin Flours with the Hydroxylated Polyamides

In order to evaluate the affinity of the hydroxylated polyamides synthesized for partially or strongly degraded waterlogged wood, preliminary tests on recent beech wood lignin samples were performed. In fact in degraded wood the cellulosic component is partially lost and the residue material is mainly formed by lignin.

Lignin samples were prepared from wood flours following standard procedures[25] and then maintained for 24 h into aqueous solutions of the consolidants and magnetically stirred at room temperature. After filtration, washing and drying at 60°C, the samples were analyzed through FTIR spectroscopy, then spectra were compared with the untreated lignin and the polyamides to evaluate the effectiveness of the treatment.

Infrared spectrum recorded on the beech wood lignin (Figure 6, spectrum c, Table I), show peaks at 1216 and 1116 cm^{-1} which are characteristic of syringyl,[26] those at 1608 and 1504 cm^{-1}

related to aromatic ring stretching[27] and the one at 1460 cm^{-1} related to CH bending.[27]

Three hydroxylated polyamides were tested on lignin samples: polyethylene-L-tartaramide, polyethylene-D(+)-glucaramide and polyethylene-α,α-trehaluronamide.

From the analysis of FTIR spectrum of lignin treated with polyethylene-L-tartaramide (Figure 6, spectrum b, Table I), it was possible to confirm the absorption of the product observing the presence of two new peaks at 1655 and 1540 cm^{-1}, related to the amidic group of the polyamide, and the decrease of the peaks at 1504 and 1216 cm^{-1}. In addition, it was possible to observe a variation in the shape of the peaks between 1116 and 1216 cm^{-1}, due to the overlapping of a peak at 1072 cm^{-1} related to the C—O stretching of the consolidant.

From the analysis of FTIR spectrum of lignin treated with polyethylene-D(+)-glucaramide (Figure 7, spectrum b, Table I), it was possible to confirm the absorption of the product observing the presence of two new peaks at 1653 and 1541 cm^{-1}, related to the amidic group of the polyamide, and the peak at 1079 cm^{-1} related to the C—O stretching of the consolidant.

From the analysis of FTIR spectrum of lignin treated with polyethylene-α,α-trehaluronamide (Figure 8, Table I), it was possible to confirm the absorption of the product observing the variation in the shape of the peak at 1660 cm^{-1}, due to the overlapping of the peaks at 1553 and 1663 cm^{-1} related to the
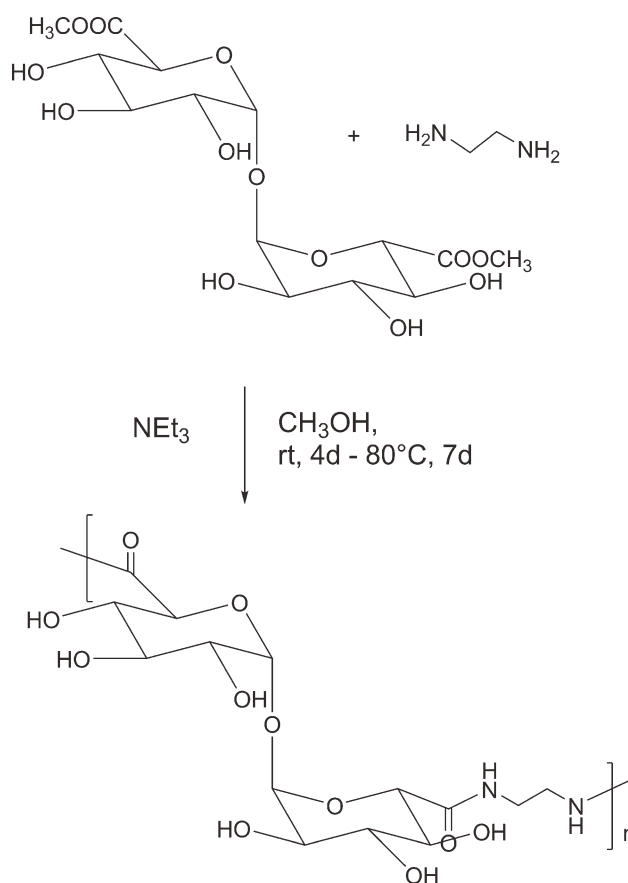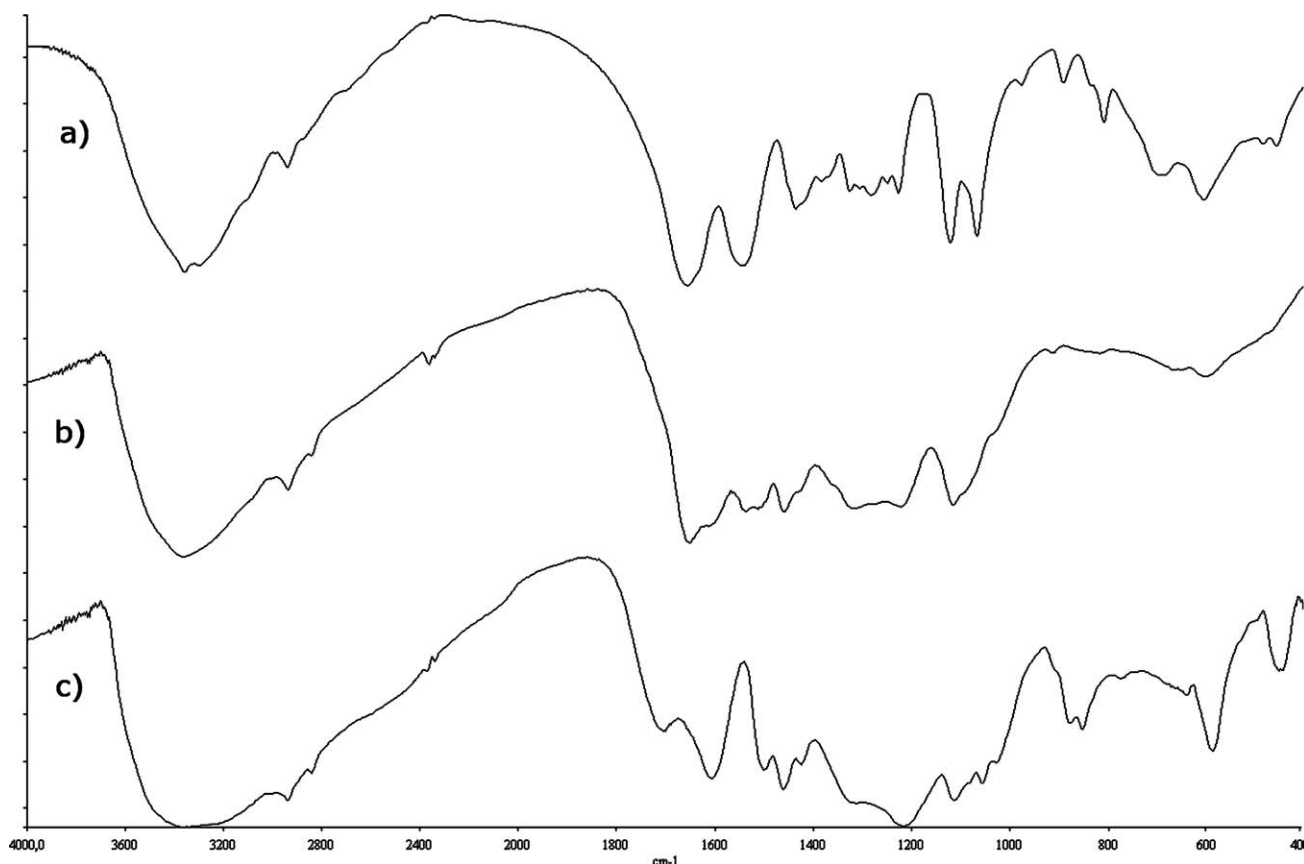

Figure 5. Synthesis of polyethylene-α, α-trehaluronamide.

Figure 6. FTIR spectra of (a) polyethylene-L-tartaramide; (b) beech wood lignin treated with polyethylene-L-tartaramide; (c) beech wood lignin.

amidic group of the polyamide. In addition, it was possible to observe the presence of new peaks at 1027, 1066, and 1104 cm^{-1}, related to the C—O stretching of the consolidant.

Reversibility of Consolidating Treatments

In order to evaluate the reversibility and the mobility of the derivatives 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, samples were analyzed again through FTIR spectroscopy and spectra compared with the ones related to the treated lignin samples.

From the analysis of FT-IR spectrum of lignin treated with polyethylene-L-tartaramide and followed by a wash, it was possible to observe that the product was partially removed. This was confirmed by the intensity decrease of the peak at 1655 cm^{-1},

the increase of the peak at 1606 cm^{-1}, the strong decrease of the one at 1540 cm^{-1}, the consequent increase of the one at 1507 cm^{-1} and the decrease of the one at 1113 cm^{-1}. However, the polyamide was partially held by lignin; this behavior was attributed to the formation of secondary interactions with wood and to the low mobility of the consolidant.

From the analysis of the FTIR spectra of lignin treated with polyethylene-D(+)-glucaramide and polyethylene-α,α-trehaluronamide and followed by a wash, it was possible to observe similar behaviours, confirming a partial retention of the consolidants by lignin.

Treatment of the Degraded Wood with the Hydroxylated Polyamides

The specimens used for the study of the physical properties of the polyamidic consolidants were recovered from an archaeological waterlogged find located in Poggiomarino, Italy.

Table I. Summary of the Relevant FTIR Transitions (cm^{-1})

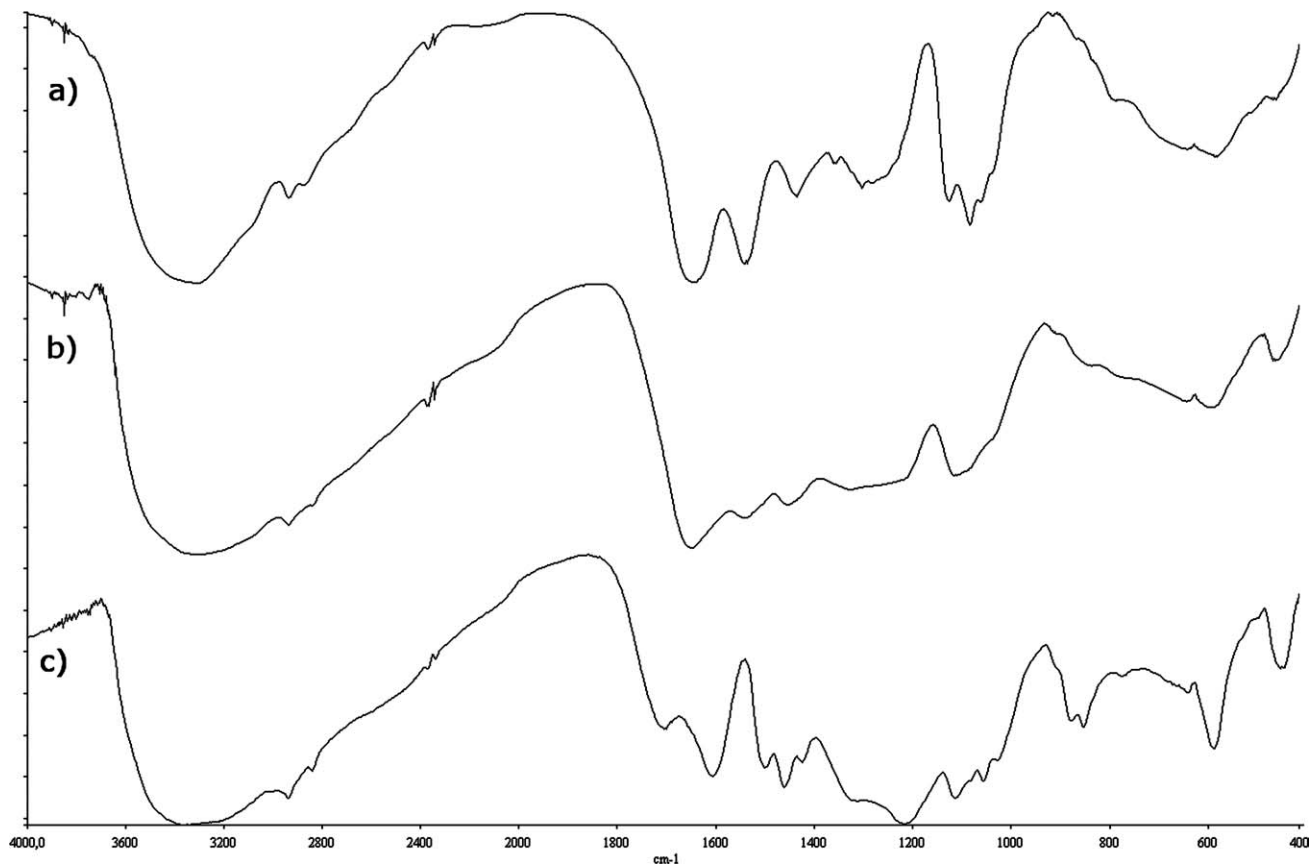|	Syringyl	Aliphatic C—H bending	Aromatic ring C—C stretching	C=O stretching	N—H bending	C—O stretching
Lignin	1116 and 1216	1460	1504 and 1608			
Polyethylene-L-tartaramide		1439		1655	1540	1072
Polyethylene-D(+)-glucaramide		1437		1653	1541	1079
Polyethylene-α, α-trehaluronamide		1415		1663	1553	1027, 1066, and 1104

Figure 7. FTIR spectra of (a) polyethylene-D(+)-glucaramide; (b) beech wood lignin treated with polyethylene-D(+)-glucaramide; (c) beech wood lignin.
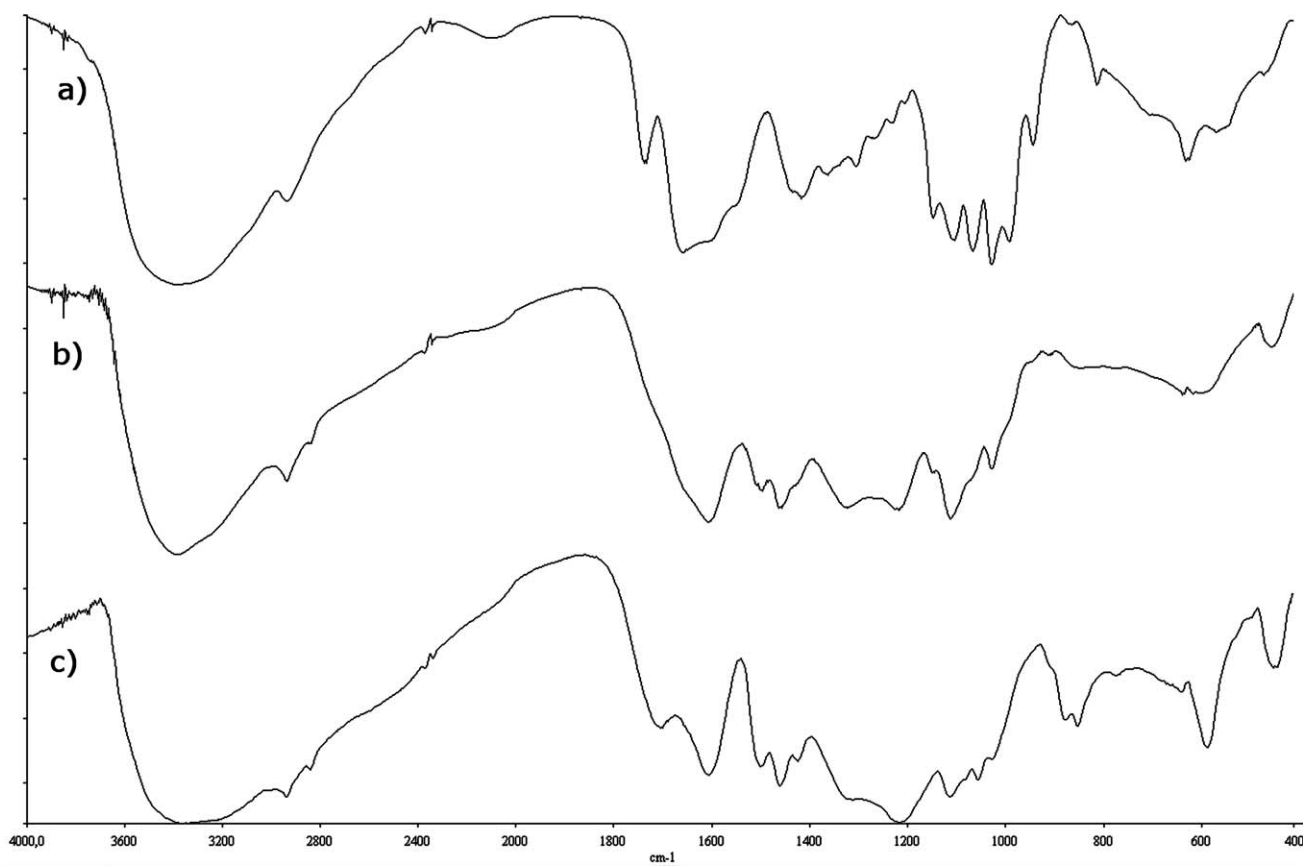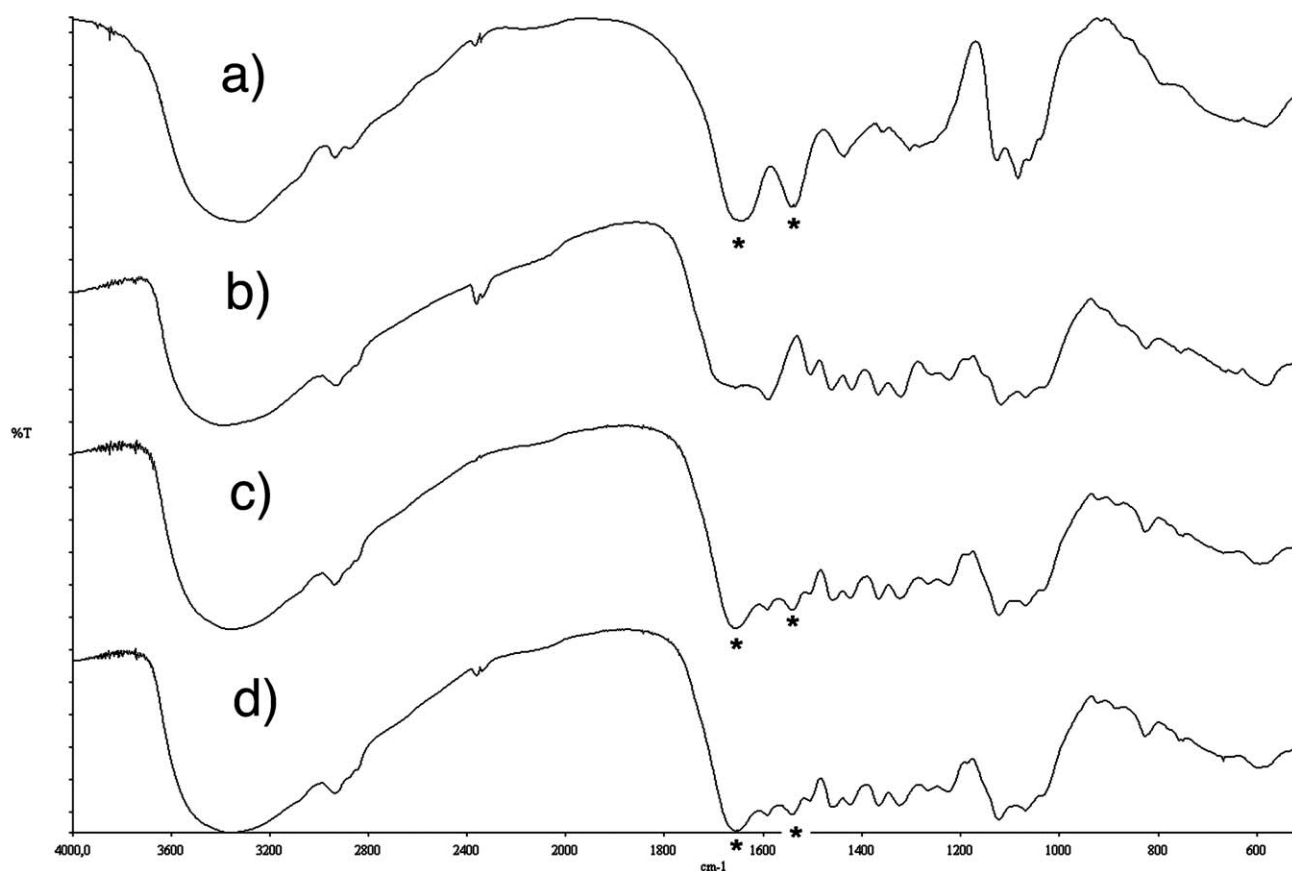

Figure 8. FTIR spectra of (a) polyethylene-α, α-trehaluronamide; (b) beech wood lignin treated with polyethylene-α, α-trehaluronamide; (c) beech wood lignin.

Figure 9. FTIR spectra of (a) polyethylene-L-tartaramide; (b) untreated archeological oak wood; (c) external section of the wood specimen treated with polyethylene-L-tartaramide; (d) internal section of the wood specimen treated with polyethylene-L-tartaramide.

Three cubic specimens obtained from the wood were subjected to consolidating treatments with polyethylene-L-tartaramide, polyethylene-D(+)-glucaramide, and polyethylene-α,α-trehaluronamide. The treatments were carried out by immersing every specimen in a solution of the consolidant and keeping it in the absence of light and at room temperature for 57 days. Then, the specimens were subjected to gravimetric and volumetric analyses to determine their physical properties.

Study of the Consolidants Penetration in the Wood
Internal and external sections were obtained from the wood specimens after the consolidating treatment. The flours obtained from these sections were analyzed using FTIR spectroscopy and compared with the untreated specimen and the polyamides. In this way it was possible to evaluate the effectiveness of the treatment by determining the presence of the consolidant on the surface of the specimens and inside them.

In fact in the FTIR spectra recorded on the wood flours obtained from the two sections after the treatment with the hydroxylated oligoamides showed the presence of the peaks attributable to polyamides. As an example, the spectra obtained after the treatment of the specimen with polyethylene-L-tartaramide, are reported in Figure 9. The presence of peaks at 1654 and 1541 cm^{-1} in the spectra of both the internal and external sections confirms the absorption and the penetration of the product.

Determination of the Specimens' Weight Variation
The determination of the specimens' weight was carried out by using the gravimetric method referring to the UNI ISO 3131 normative.[23] This method allowed to evaluate the weights of the specimens treated with the different consolidants at relative humidities (R.H.) of 100, 86, 65, and 12%. At first, the treated specimens were washed with demineralized water to remove the excess of consolidant on their surface. For the determination of

Table II. Weights of the Specimens at Different R.H. Values (g)

Wood sample	I.H.	100%	86%	65%	12%
Polyethylene-L-tartaramide	1.1932	1.0537	0.4328	0.4115	0.3636
Polyethylene-D(+)-glucaramide	2.4578	1.5934	0.861	0.8175	0.7288
Polyethylene-α, α-trehaluronamide	1.5845	0.9857	0.5136	0.4802	0.4242
Reference wood (untreated)	1.460	1.2439	0.4168	0.386	0.3355

Table III. Moisture Content of the Specimens at Different R.H. Values

Wood sample	I.H. (MWC)	R.H. 100%	R.H. 86%	R.H. 65%
Polyethylene-L-tartaramide	228%	190%	19%	13%
Polyethylene-D(+)-glucaramide	237%	119%	19%	12%
Polyethylene-α, α-trehaluronamide	274%	132%	21%	13%
Reference wood (untreated)	335%	271%	24%	15%
Recent wood	80%	30%	18%	12%

the initial humidity and the volume, the specimens were weighed and cubed with the water displacement method. Then they were placed in a desiccator containing demineralized water and kept there until the environment was saturated with water vapors (R.H. 100%). Then, every specimen was weighed and introduced again in the desiccator. The weighings were repeated until the weight variation observed was lower than 1%. The weight stabilization was an evidence of the reached hygroscopic equilibrium of the specimens in the desired environmental conditions. Subsequently, the stabilization of the specimens at R.H. 86% and 65% was carried out. For the tests at R.H. 86%, the specimens were placed in a desiccator containing a saturated solution of potassium chloride (as indicated by the normative ISO 483[28]) in order to keep the R.H. value consistent. For the tests at R.H. 65%, the specimens were placed in a desiccator containing a saturated solution of ammonium nitrate (as indicated by the normative ISO 483[29]) in order to keep the R.H. value consistent. The balance used for the weighings had a resolution of 10^{-3} g and it was placed in a climatized box at a temperature of 20°C and at the same R.H. of the desiccator. Also in this case the weighings were repeated until the specimens reached a constant weight.

The specimens, once equilibrated at R.H. 65%, were weighed and placed in an oven at 50°C for 24 h to favor the loss of humidity. The corresponding R.H. was 12%, and in these conditions the comparison between the untreated and the treated specimens was made. The temperature used was different from the one reported by the normative UNI ISO 3131[28] (103°C), corresponding with the anhydrous state (R.H. 0%), in order to keep the temperature far from the T_g of the consolidants. After 24 h the specimens were removed from the oven and placed in a desiccator, cooled to room temperature, and weighed again. This procedure was repeated until the specimens reached a constant weight. The determination of the weight at the anhydrous state allowed to calculate the wood moisture content in

the initial conditions (I.H.) and at the three hygroscopic equilibrium values (R.H. 100%, 86%, 65%) and to evaluate the basic density. For this purpose in this study, the measurement conditions at R.H. 12% were considered equivalent to those at the anhydrous state. The absolute weights at the different R.H. values are reported in Table II.

The results related to the moisture content of the wood at different R.H. values are reported in Table III.

From the data analysis it was possible to observe how all the examined samples had higher moisture content with respect to the recent oak wood. The higher hygroscopicity of archaeological wood is caused by the partial or total loss of the crystalline structure of cellulose, which leads to an increase of the sites available to create bonds with water molecules. In the treated specimens the consolidants limited this phenomenon, saturating most of the hydroxyl groups of the wood. For this reason, in all the treated specimens the moisture content appeared to be lower respect to the untreated wood.

Determination of the Volumic Mass

The determination of specimens' volumic mass was carried out by weighing every specimen and calculating the volume through the water displacement method. The results of the measurements performed on the three specimens and on the reference sample at R.H. 12% are reported in Table IV.

The volumic mass values calculated at different moisture contents of wood are reported in Table V.

In general, archaeological wood has a volumic mass lower than recent wood, due to the loss of material, in a different entity depending on its degradation state. In fact, comparing recent wood with archaeological wood this difference can be clearly noticed. The comparison with the volumic mass values of the samples treated with the consolidants showed instead a slight variability.

Table IV. Volumic Masses of the Specimens at R.H. 12%

Wood sample	Volume (cm^3)	Weight (g)	Volumic mass (g/cm^3)
Polyethylene-L-tartaramide	0.640	0.3636	0.568
Polyethylene-D(+)-glucaramide	1.377	0.7288	0.529
Polyethylene-α, α-trehaluronamide	0.756	0.4242	0.561
Reference wood (untreated)	0.623	0.3355	0.538
Recent wood	–	–	0.8

Table V. Volumic Masses of the Specimens at Different R.H. Values

Wood sample	I.H.	R.H. sat.	R.H. 65%
Polyethylene-L-tartaramide	1.136	1.075	0.508
Polyethylene-D(+)-glucaramide	1.127	0.817	0.500
Polyethylene-α, α-trehaluronamide	1.124	0.516	0.358
Reference wood (untreated)	1.157	0.651	0.364
Recent wood	–	1.050	0.740

Table VI. Basic Densities of the Specimens

Wood sample	Basic density (g/cm^3)
Polyethylene-L-tartaramide	0.319
Polyethylene-D(+)-glucaramide	0.306
Polyethylene-α, α-trehaluronamide	0.269
Reference wood (untreated)	0.206
Recent wood	0.690

Determination of the Basic Density

The results related to the basic density (Table VI) showed how the consolidants were penetrated into the wood, leading to an increase of the density respect to the untreated wood.

Determination of the Volumetric Shrinkage

The volumetric shrinkage of the specimens were calculated through the water displacement method in both conditions. In detail, for the anhydrous samples, very fast weighings were carried out in order to minimize the water absorption.

The results are related to the volumetric variations that the specimens showed in the humidity range comprised between R.H. 12% and MWC (maximum water content). The results are reported in Table VII.

CONCLUSIONS

Hydroxylated oligo- and polyamides were synthesized in order to use them as new consolidants for waterlogged wood. The diacids used in the polycondensation reactions were obtained from renewable resources. In fact natural compounds or their derivatives, as L-tartaric acid, D(+)-glucaric acid, and α,α-trehaluronic acid were used as diacids in the polycondensation reactions with 1,2-ethylenediamine, obtaining oligoamides with different molecular weight and different hydrophilic/hydrofobic ratio.

Three water-soluble hydroxylated polyamides, polyethylene-L-tartaramide, polyethylene-D(+)-glucaramide, and polyethylene-α,α-trehaluronamide, were tested as consolidants for wood using a new diagnostic protocol. Impregnation tests carried out using archaeological wood flours or lignin and monitored with FT-IR spectroscopy showed a high affinity of the new consolidants for lignin, in agreement with a possible use for degraded wood. The penetration of the consolidants and the physical properties of wood, as hygroscopic equilibrium, basic density, and dimensional stability, evaluated using small archaeological wood samples appear very interesting. The time needed to achieve the hygroscopic equilibrium at different relative humidity values was comparable for all the products, and the moisture value of the samples at RH 65% was satisfactory respect to the one of recent wood. The penetration of the consolidants was confirmed using FTIR spectroscopy for the analysis of the internal and external sections of the specimens.

The dimensional stability of wood was then estimated by evaluating the volume shrinkage and a good behavior of all samples treated with polyamides was observed.

In conclusion the hydroxylated oligoamides were identified as products of interest for the development of new consolidants.

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Table VII. Volumetric Shrinkages of the Specimens

Wood sample	Volumetric shrinkage (%)
Polyethylene-L-tartaramide	43
Polyethylene-D(+)-glucaramide	39
Polyethylene-α, α-trehaluronamide	49
Reference wood (untreated)	60
Recent wood	18

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