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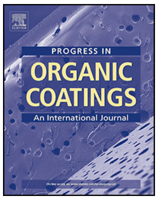

Hybrid organic–inorganic materials as coatings for protecting wood

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ABSTRACT

A new coating based on organic–inorganic materials was prepared using concurrent sol–gel and polymerization techniques, and applied to wood using a dip coating method. Vinyl-functionalized zirconium oxoclusters were co-polymerized with vinyltrimethoxysilane on wood. The coating process was examined, also assessing the specific weight of hybrid polymer left on the wood after one or two coating steps. The efficacy of the process in consolidating and protecting the wood was investigated using high-temperature differential scanning calorimetry (DSC), environmental scanning electron microscopy (ESEM), infrared spectroscopy and solid state NMR spectroscopy. The coating did not affect the morphology and appearance of the wood. However, it did modify its behavior on exposure to fire and preliminary accelerated biological tests with the brown rot fungus *Coniophora puteana* showing an improved resistance to the fungal attack.

1. Introduction

Wood is strongly affected by the environment. Insects primarily attack wood and moisture is known to promote the growth of fungi, which increase the wood's permeability and water adsorption. In order to minimize these effects and also the rate of combustion or delay ignition, chemical treatments can be applied to wood. In this study, a new coating made with organic–inorganic materials was prepared using concurrent sol–gel and polymerization techniques. It was applied to wood with a dip coating method. Accordingly, the behavior of the coated wood exposed to fire and fungi was investigated. The preparation of the coating is described, starting from the precursors' sol of vinyltrimethoxysilane (VTMS) in tetrahydrofuran (THF) and zirconium oxoclusters.

As general rule, in sol–gel process alkoxysilanes react with water with either an acid or a base as catalyst. The species resulting from hydrolysis condense forming polysiloxanes and, in order to increase condensation, the gel can be subjected to an additional thermal treatment. When alkoxysilanes are used for coating wood, the hydroxyl groups of cellulose, hemicellulose and lignin can act as binding site and facilitate the adhesion of gel [1,2]. The hydrolysis/condensation process occurs in situ, by using the water adsorbed onto cell walls of wood. Studies have shown that if hydrolysis/condensation start before the penetration into cells, the treatment results less effective, because the gel adheres mainly to lumina, being more viscous [1,3,4].

The use of alkoxysilane approach to protect wood has several advantages, such as high availability of the raw materials, low cost, limited toxicity and the opportunity to control the rate of hydrolysis. An alternative approach involves inorganic material in the form of metal oxide [5–9], spread onto wood as additives into oil/wax finishes or directly as a thin film deposited by sol–gel process, typically titanium oxide [10–13], which resulted able of retarding the combustion of the wood matrix.

Alkoxysilanes and metal oxides (aluminum, iron, zirconium and zinc oxides) [14–16] have also been used together in organic–inorganic hybrid thin films, which have revealed positive effects in preserving the wood's natural color and stabilizing the wood against sunlight and moisture-related degradation.

Given the virtually unlimited number of combinations of organic and inorganic components, there are countless organic–inorganic materials, and many are potentially suitable for applications as coatings on different substrates [17–22]. Several examples of protective coatings for wood are described in the scientific and patent literature [21–32]. Like protective coating on paper, they must have at least three important features, i.e. they must be transparent, they must preserve the esthetic features of the underlying material, and they must have a high elastic modulus. Several published studies describe applications of hybrid materials based on sol–gels, which give wood antibacterial properties [4] as well as improving its fire, weather, chemical and water resistance [33,34]. There is also a growing interest in hybrid materials in which various metal

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oxide nanoparticles MO_x (M = Ag, Ti, Zn, Al) are embedded, for use in protecting wood against fire, humidity and sunlight [34,35].

The inorganic building block used in this work is the well-known and well-characterized zirconium dodecanuclear oxocluster $[Zr_6O_4(OH)_4(VyAc)_{12}(nPrOH)]_2{\cdot}4(VyAcH)$ [36,37]. This oxocluster reacts with VTMS forming a new hybrid monomer, which in presence of a polymerization initiator, such as benzoyl peroxide (BPO), is able to polymerize, although to a small extent, forming a hard and resistant material [36,37], which meets the requirements of transparency and stiffness, without altering the esthetic features of wood.

The outbreak of a fire is one of the most unpredictable and dangerous accidents that can occur especially in residential buildings, even for a wood that behaves well when exposed to fire, the effects of which are highly complex. Fire retardant treatments applied to wood generally contain the effects of a fire, preventing flame propagation and the amount of smoke generated. Any flammable material first needs to be ignited. When a surface is exposed to a heat flux, most of the heat is initially transferred inside the material. The rate of this heat transfer depends on the material's properties. When the surface temperature of wood exceeds 300–350 °C, a small pilot flame or spark is enough to ignite a fire, and a char layer forms immediately afterwards. After ignition, the heat release rate is high because volatiles easily spread through the surface layer. In this study, tests with the cone calorimeter were used to assess how the coatings being tested contributed to the heat release rate when the coated wood was exposed to fire, and small-flame tests were used to ascertain its ignitability when a small flame impinged directly on the wood.

The morphology of the coated substrates was examined using environmental scanning electron microscopy (ESEM). After the wood coating had been characterized, accelerated biological tests were run with the brown rot fungus *Coniophora puteana* (one of the most aggressive fungi that attack softwood in Europe) to ascertain the antifungal efficacy of the protective coatings.

2. Experimental

2.1. Materials

Different larch and pine wood boards (510 mm × 74 mm × 17 mm) were prepared in a static humid chamber at three moisture levels for the larch, i.e. 6%, 12% and 14% of relative humidity (RH), and one for the pine, at 12% RH. The wood specimens were cut in the radial direction and, immediately after a surface refreshing treatment, coated by soaking them in a hybrid sol.

2.2. Sol preparation

Vinyl acetic acid (VAA) and zirconium n-propoxide were used without further purification, mixed in a molar ratio of 4:1 under an N_2 atmosphere at room temperature and left to stand until the precipitation of crystals. After separation, they were dissolved in THF and VTMS was added to the solution, with the molar Zr:Si ratio of 1:10. Benzoyl peroxide (BPO, 1 wt% of VTMS and crystals) was lastly added as polymerization initiator [36–40].

2.3. Preparation of the coated wood samples

The wooden samples were coated by dipping them in the hybrid organic–inorganic material. They were submerged in the sol for 20 min. The solvent was left to evaporate at atmospheric pressure for 20 min, then the samples were cured in an oven at 90 °C for 30 min. Each sample was weighed before and after completing the dipping, solvent evaporation and heat treatment stages in order to establish the amount of coating absorbed by the wood.

Two sets of coated samples were prepared: the first (series I) was cured immediately after dipping, leaving a coating of about 50 g/m^2; the second (series II) was dipped in the solvent twice to increase the protective coating to 120 g/m^2. Series II was mainly prepared for the cone calorimeter test (both larch and pine at 12% RH) and the fungal test (pine at 12% RH).

2.4. Instrumentation

A Philips XL-30 environmental scanning electron microscope was used to study the samples' morphology and surface topography. Energy-dispersive X-ray spectroscopy (EDXS) analysis was also used to investigate the chemical composition of the materials. High-temperature differential scanning calorimetry (HT-DSC) was performed with the HT-DSC SETARAM, in air (100 ml/min), with a 10 °C/min heating rate.

Solid state ^{29}Si MAS NMR spectra were recorded at room temperature with a Bruker Avance 400 WB NMR spectrometer operating at a carrier frequency of 400.13 MHz (^{1}H) equipped with a double resonance 4 mm magic angle spinning (MAS) probe. Coated chips wood and the corresponding gel were placed in 4 mm zirconia rotors and spun at 6 kHz. The ^{29}Si experiments were based on cross polarization sequence with proton decoupling (CP-MAS) under the following conditions: a 90° pulse length for protons of 3.60 μs, a contact time of 5 ms and a recycle delay of 10 s. The peaks are described according the conventional chemical notation for the siloxane structure: the capital letter represents the number of hydrolysable groups (i.e. T for trifunctional silicon), and the superscript indicates the number of oxobridges.

Fourier transform infrared spectra (FTIR) were recorded in reflectance mode (ATR system with a zinc selenide crystal) in the range of 4000–650 cm^{-1}, using a Perkin Elmer Spectrum One. The spectra were recorded with a resolution of 2 cm^{-1}, with each spectrum averaged over 64 scans. All stack spectra were normalized and baseline corrected before plotting to facilitate their comparison.

The larch wood samples were irradiated in air in a xenon test chamber (Solarbox 1500e), using a xenon-arc lamp designed to simulate the full solar spectrum (wavelength: $300 < \lambda < 400$ nm, irradiance: 0.35 W/m^2/nm). The samples were placed 28 cm away from the light source. The temperature and humidity were controlled at 21 ± 3 °C and 60 ± 1% RH during irradiation. The samples were exposed for different periods of time, ranging from 1 day to 24 weeks. Color variations were measured ten times for each sample using a Konica Minolta (CM-2600d) spectrophotometer, recording the lightness (L^*, where 0 is black and 100 is diffuse white) and the color-opponent dimensions (*coordinates* a^* and b^*), where negative values of a^* indicate a shift toward green and positive values indicate a shift toward magenta, while negative and positive values of b^* indicate a shift toward blue and yellow, respectively.

Two fire test methods were adopted. For the first, the samples of wood were tested in a laboratory-scale apparatus in accordance with the Italian UNI standard 8457:2008 (*Combustible products liable to direct contact with fire on one surface: reaction to fire on applying a small flame*), in which a small flame impinges directly on a specimen to assess its ignitability. Larch specimens (prepared at 6%, 12%, 14% RH, cut in the radial direction to 70 mm × 40 mm × 1.4 mm in size) were placed vertically in a U-shaped specimen holder and a propane gas flame 20 mm in height was brought into contact with the specimen for 30 s at an angle of 45°. If ignition occurred, we recorded flame propagation along the specimen, the duration of flaming and glowing, the dimensions of the area damaged, and whether flaming particles fell from the product, and the sample was classified according to criteria based on these observations. Five specimens were tested for each RH level used to prepare the larch samples.