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Photocurable resin/nanocellulose composite coatings for wood protection

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ABSTRACT

Novel UV-light curable methacrylic-siloxane-cellulose composite coatings for wood protection were prepared, fully characterized and, then, applied on walnut wood samples in order to assess the potential protective performances of the wooden treated substrates, such as hydrophobicity and surface properties. A comparison between nanocellulose and microcellulose filled coatings (5 and 10 wt%) was also performed. Thermal-mechanical analysis highlighted the higher effectiveness of nanocellulose in increasing the glass transition temperature, improving thermal and dimensional stability and stiffness of the neat photoresin with respect to microcellulose. A more pronounced increase of hydrophobicity (contact angle and water capillarity), surface hardness (Shore D and pencil scratch tests) of the neat UV-light cured matrix filled with nanocellulose and applied on wood was, finally, observed in comparison to microcellulose composites.

1. Introduction

Wood is one of the most used and abundant renewable material in the world. It is utilized for a wide of applications, but its main drawback is the high propensity to decay for various degradative processes [1]. The degradation of wood in artworks and buildings is still an open issue. Environmental agents and microbial attacks combined to the water action are the main causes of wood's decay [2]. In fact, the most frequent and dangerous degradation phenomena are correlated to the presence of water, that can act as a medium to convey aggressive agents or alone, causing internal stresses due to pressure and temperature changes. The capillary rising, for instance, is the most widely phenomenon visible on the facades of the buildings, especially those built with porous wood. These materials have, in fact, a very complex structure, that promotes water absorption by capillarity [3]. Furthermore, biological degradation is very frequent for wood substrates and their repair is still an open issue. In fact, some wood types are very sensitive to biological attacks, due to their microstructure and porosity. All these chemical, physical and/or mechanical degradative processes are catalyzed by the water presence and the overall effect is to impair the mechanical properties of wood [4,5].

Thermal or chemical treatments and impregnation modification have revealed good prospective in reducing water absorption and deformation, rising biological resistance and improving weathering performance [6]. In details, linear anhydrides, aldehydes, furfuryl alcohol,1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), phenolic or melamine resins, could be considered the most efficient treatments to increase the durability of wood substrates [7,8].

Polymers based on acrylic and metacrylic monomers are extensively used for the protection and conservation of wood, too [9]. Acrylic based coatings, however, have shown durability issues for the protection of outdoor buildings for long time [10–12]. Acrylic coatings generally manifest a reduced adhesion on porous substrates and offer a certain drainage of water from the treated surface [8,13–15].

In addition, most common wood protectives, such as nitrocellulose lacquer, polyurethane, unsaturated polyester and amino acid curing [16], are solvent-based coatings containing volatile organic compounds (VOCs). Some products contain benzene, toluene, xylene, and substances of great carcinogenicity, which could damage the environment and human health. Environmentally friendly coatings, such as high-solid-content, waterborne, radiation-curable or powder coatings could substitute the solvent-based coatings

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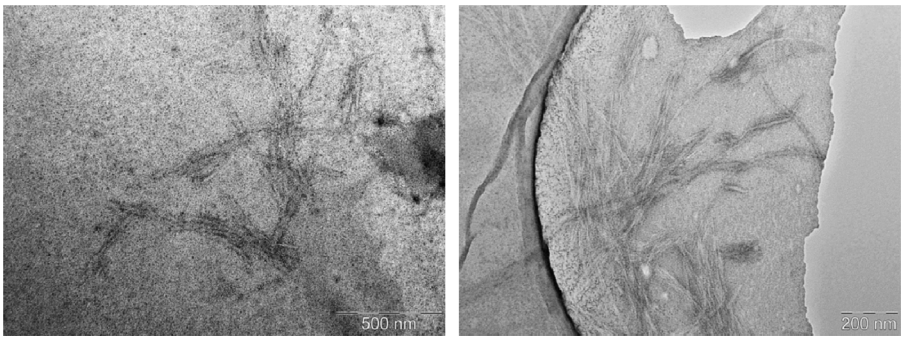

Fig. 1. TEM images of CNC particles isolated from CMC by acid hydrolysis.

[17,18]. In addition, the use of UV-curable wood coatings contributed to the growth of environmentally friendly coatings. UV curing has now been recognized as a substitute curing method to thermal one. The photopolymerization reaction allows a fast chain growth curing reaction, by using photon energy from radiation sources. Furthermore, UV-curable coatings possess superior durability, chemical and stain resistance, as well as faster reaction rates and substantial reductions, or complete elimination, of VOCs [19–23]. There is an increasing attention on the use of cellulose-based fillers as renewable reinforcing agents in order to replace the standard synthetic fillers. In this work the cellulose nanocrystals (CNC) were selected as nanoscale filler.

CNCs are isolated through the acid hydrolysis of natural cellulose fibers [24] or from already hydrolyzed cellulose microcrystals (CMC) [25]. In fact, rod-like CNC particles have interesting properties, in terms of biocompatibility, anisotropy, good optical transparency, low thermal expansion coefficient and, especially, high elastic modulus, similar to steel [26,27].

Interestingly, even if cellulose is a hydrophilic polymer it can promote an increment of the barrier properties of polymeric matrices when dispersed at a nanoscale level [13,28]. In fact, cellulose nanocrystals can produce a reduction of the diffusivity of penetrant liquids thanks to an increase of tortuosity provided by their bonding with the polymer chains [29]. Additionally, the chemical affinity between wood and cellulose-based fillers and the promising preliminary results obtained by the photoresin filled with cellulose microcrystals (CMC) [23] have encouraged the investigation of this nanofiller.

Therefore, the purpose of this work is the development, characterization and application of photopolymerizable siloxane-methacrylic-based resin/CNC, specifically intended for the surface and barrier protection of wood substrates. The comparison between micro- and nanocomposites was performed as well. The nano and microstructured UV cured coatings, obtained by the inclusion of both CNC and CMC, are evaluated as protective coatings on wood with improved performances (i.e. surface properties and hydrophobicity).

2. Experimental

2.1. Matrix synthesis and CNC isolation

The basic components and their content into the formulation of the neat photomatrix are listed below:

- Trimethylpropane trimethylacrylate (TMPTMA), provided by Sigma Aldrich (St. Louis, MO, USA) at 85 wt%;
- Trimethoxypropyl silane methacrylate (MEMO), provided by Dow Corning (Midland, MI, USA) at 10 wt%;

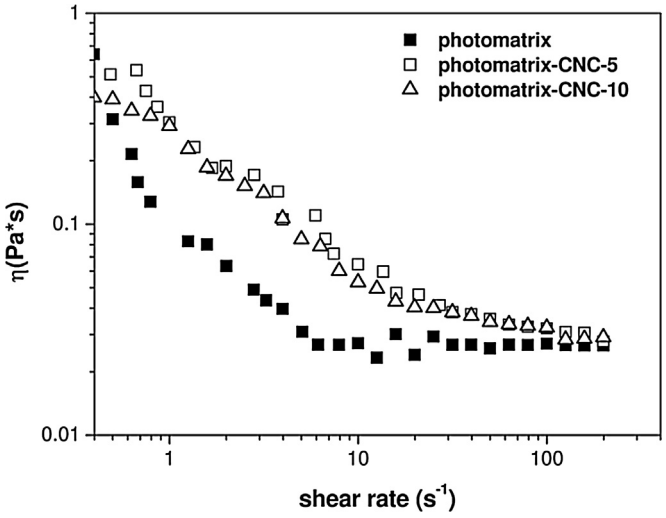

Fig. 2. Apparent viscosity of neat photomatrix and its corresponding nanocomposites.

- Poly(dimethylsiloxane)-terminated vinyl (VTPDMS), supplied by Sigma Aldrich at 4.97 wt%;
- Alkoxy- silane compound (MPTS), supplied by Sigma Aldrich at 0.03 wt%;
- Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, supplied by Ciba as IRGACURE 819 (1 pph), was used as photoinitiator.

The synthesis procedure, the composition of the photo-resin and chemical formula of all components are reported in previous works [23,30].

Microcellulose (CMC), specific gravity of 1.56 g cm^{-3}, a mean molecular weight of 90.000 g/mol, average aspect ratio of 2.4 as purchased from Sigma Aldrich, USA. Aqueous suspensions of cellulose nanocrystals were obtained through the sulfuric acid hydrolysis of microcellulose according to the method described by Bondeson-Oksman and Cranston-Gray [31,32] with minor modifications. The acid hydrolysis was carried out at 45 °C under vigorous stirring for 120 min, using a 64% w/w sulfuric acid solution, a CMC/acid ratio of 10 g/100 ml and a mechanical mixer. A CMC amount of 20 g was processed each time. The reaction was stopped adding 10 folds distilled water. The acid was removed by two centrifuge cycles at 6000 rpm for 15 min each one. The pH of suspension was neutralized through dialysis using cellulose membranes with a cut-off limit of 3.5 kDa. The suspension was then sonicated for 5 min with a Hielscher UP400S device equipped with a cilindrical sonotrode 3 mm in diameter. An average concentration of about 1.4 wt% of CNC in the suspension was determined by TGA analysis in an isothermal test at 120 °C for 20 min under a nitrogen flow of 100 ml min, in order to allow the complete removal of the sol-