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Photocurable resin/microcrystalline cellulose composites for wood protection: Physical-mechanical characterization

Annalisa Cataldi[a], Carola Esposito Corcione[b], Mariaenrica Frigione[b], Alessandro Pegoretti[a,*]

[a] University of Trento, Department of Industrial Engineering and INSTM Unit Via Sommarive 9, Povo 38123, Trento, Italy
[b] University of Salento, Department of Innovation Engineering, Via Monteroni, 73100 Lecce Italy

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ABSTRACT

Photocurable composites based on a UV-light curable methacrylic-siloxane resin formulation and various concentrations (5 ÷ 20 wt%) of microcrystalline cellulose powder (MCC) were prepared and characterized to assess their suitability as protective coatings for wooden artworks. Dynamic mechanical thermal analysis highlighted that MCC promoted an enhancement of both storage and loss moduli and a decrease of the thermal expansion coefficient. Interestingly, the flexure elastic modulus and the flexure maximum stress of the neat photoresin increased upon the filler addition without any embrittling effect. An increment of hydrophobicity (contact angle), surface hardness (Shore D and pencil scratch tests) of the neat UV-light cured matrix even at the lowest filler loading was observed. These promising results suggest that the photo-curable microcomposites could be able to recover the mechanical and physical properties of damaged wood and replace the traditional resins soluble in toxic solvents utilized in this kind of restoration works.

1. Introduction

Wood is one of the most common constituent materials of cultural heritage. It was one of the first materials utilized for building. Wood was widely used in the past for outdoor and indoor purposes, to make artworks such as eating utensils, decorations of buildings and churches or egg-based paintings. This material is very sensitive to decay and several degradative processes can attack it [1].

Chemical, physical, biological or mechanical decay leads to similar effects on wood, in particular promotes the reduction of its mechanical strength [2,3]. In order to recover wooden artworks subjected to a critical degradation state, conservators choose to protect and consolidate objects by the application of a liquid synthetic resin through brush, spray, injection or the direct immersion [4,5]. In particular, Paraloid B72 is certainly one of the most utilized protective materials for damaged wood because it guarantees good performances [6]. A typical wood restoration treatment with Paraloid B72 consists of the application by brush of solutions at 3–10 wt% of this acrylate in acetone or even stronger and toxic solvents. A possible and promising solution to this drawback could be the application of curable monomers/oligomers, that, having a lower viscosity with respect to polymers, do not require the use of solvents. Recently, Cataldi et al. have successfully produced microcomposites consisting of Paraloid B72 filled with MCC. The Paraloid/MCC composites were characterized and tested as protective materials for hystorical damaged wood samples with positive results [7,8]. In fact, cellulose based fillers are more and more utilized in the wood protection [9,10]. In particular, MCC was selected for its well-known reinforcing properties [11,12] and its chemical affinity with wood having the same chemical composition. Moreover, MCC is easy to source, conservators can handily use it because it does not require any other chemical process to be applied.

Corcione et al. have characterized curable formulations based on siloxane and methacrylic or acrylic monomers in terms of adhesion on surfaces, hydrophobicity, optical transparency, capability to prevent infiltration of contaminants or degrading agents, permeability to water vapor, chemical compatibility with different inorganic substrates, finding excellent antifouling and weathering resistance [13,14]. The low molecular weight of the monomers, the low viscosity of the formulation, as well as the in situ polymerization mechanism, allow the resin penetration inside porous substrates, such as stones or wood, leading to a uniform and very adherent hydrophobic coating [13]. Such properties make them optimal materials for manufacturing water repellent and optically

* Corresponding author.
E-mail addresses: annalisa.cataldi@unitn.it (A. Cataldi), alessandro.pegoretti@unitn.it (A. Pegoretti).

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clear coatings for protection and conservation of wood, stones and concrete buildings, lens, dental elements and adhesives and multifunctional finishing agents for textiles and leather components [15]. Guo et al. have utilized a UV-light photoinitiator for activating photopolymerization of formulations based on such monomers as a valuable alternative to the thermally initiated curing [16], that is an approach typically used for preparing coatings for protection of natural stones or wood artworks. UV-light photoinitiation is a solvent-free curing mechanism based on a photopolymerization faster than that activated by a thermal initiator [15]. Indeed, thermal curing requires up to several weeks to complete the reaction, and, hence, it is strongly affected by environmental conditions (i.e. temperature, humidity and external contamination). The fast UV curing process results, especially in outdoor and large surface area applications, in highly adherent, stable and, completely cured coatings, exhibiting a glass transition temperature (Tg) higher than those achieved by means of thermal polymerization or by solution processes, whose Tg anyway never exceeds 40 °C.

In the present work the introduction of microcrystalline cellulose into a UV-light curable methacrylic-siloxane resin formulation (photoresin) is considered for a potential improvement of its performances as protective coating for wood. The photoresin, recently optimized by the authors, is based on both methacrylic and siloxane monomers, namely trimethylolpropane trimethacrylate (TMPTMA), (trimethoxysilyl)propylmethacrylate (MEMO) and a vinyl terminated polydimethylsiloxane (VT PDMS), that are UV-light photoinitiated by Irgacure819. This work represents the preliminary characterization of photocurable composites filled with microcrystalline cellulose, in view of the application of these materials as protective coatings on degraded wood.

2. Experimental

2.1. Materials

Trimethylolpropane trimethacrylate (TMPTMA) was chosen as the main component for the coating due to its high reactivity. The product used was supplied by Cray Valley.

A trimethoxypropyl silane methacrylate monomer, produced by Dow Corning as Z6030 and known as MEMO, was used as a coupling agent.

A vinyl terminated polydimethylsiloxane (VT PDMS), supplied by Aldrich, was added to the methacrylic mixture to enhance the coatings' water resistance.

A 3-mercaptopropyltriethoxysilane (MPTS), supplied by Aldrich, was added to the siloxane modified methacrylic resin system in order to reduce the effect of inhibition of oxygen towards radical photopolymerization. MPTS has an average molecular weight of about 238.42 g/mol.

The functionalization of VT PDMS with MPTS was done by mixing the two components at 100 °C in 1:1 molar ratio in presence of 1% wt. of diethylamine (DTA), again supplied by Aldrich. The chemical formula of all components are reported in Fig. 1.

Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, supplied by Ciba as IRGACURE 819, was added to the polymeric formulation in a content of 1 pph to activate the photopolymerization reaction upon UV exposure.

Microcrystalline cellulose powder (MCC) (Sigma Aldrich, USA) with a specific gravity of 1.56g cm^{-3} and a mean molecular weight of 90.000 g/mol was selected as a filler.

2.2. Preparation of UV-curable microcomposites

Composites with a MCC amount from 5 wt% to 20 wt% were prepared through the mechanical mixing of the photoresin with the microfiller under magnetic stirring at room temperature. All formulations were poured in the cavities of silicon molds and introduced into a UV-chamber equipped with six UVB lamps model UVB 313EL (Q-lab corporation, UK) with a maximum peak of emission centered at 315 nm and a total power of 480 W. A curing cycle of 24 h was conducted. Samples for mechanical tests were conditioned at 23 °C and 55% of relative humidity in a chamber with a super saturated solution of $Mg(NO_3)_2{\cdot}6H_2O$ until the reaching of the equilibrium conditions. This is the indoor humidity level recommended for the optimal artwork conservation and fruition [17]. Composites samples were denoted indicating the photomatrix, the filler (MCC) and its weight concentration. The compositions of the experimental formulations produced is outlined in Table 1.

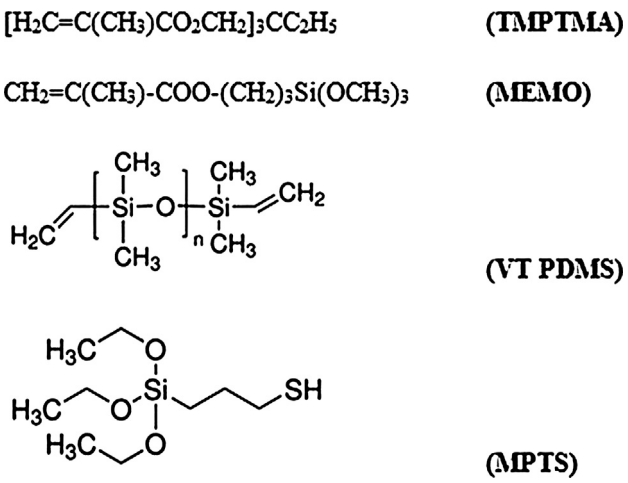

Fig. 1. Chemical formula of the photomatrix constituents.

Table 1
Composition of the experimental formulations produced.

System	Weight percentage (% wt.)
photomatrix	85% TMPTMA 4.97% VTPDMS 0.03% MPTS 10% MEMO
photomatrix-MCC-5	95% photomatrix 5% MCC
photomatrix-MCC-10	90% photomatrix 10% MCC
photomatrix-MCC-20	80% photomatrix 20% MCC

2.3. FESEM analysis

Microstructural observations on cryofractured surfaces of the neat photomatrix and the corresponding microcomposites samples were carried out by a Zeiss Supra 40 high resolution FESEM microscope with an accelerating voltage of 1.5 kV and a beam aperture of 20 μm.

2.4. Rheological tests

The rheological characterization of each liquid formulation was carried out in a strain controlled Rheometer (Ares Rheometric Scientific). The tests were performed with a plate/plate geometry (radius = 12.5 mm) under steady state mode, at room temperature (25 °C) using a shear rate ranging from 0.05 to 100 s^{-1}. A first sweep experiment was always followed by a second one performed