Progress in Organic Coatings 125 (2018) 153–159

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Facile one-step fabrication of highly hydrophobic medium density fiberboard (MDF) surfaces via spray coating

Pedro Henrique Gonzalez de Cademartori[a,b], Wido Herwig Schreiner[b], Washington Luiz Esteves Magalhães[b,c,*]

[a] Departamento de Engenharia e Tecnologia Florestal, Universidade Federal do Paraná, Curitiba 80210-170, Brazil
[b] Programa de Pós-Graduação em Engenharia e Ciência dos Materiais (PIPE), Universidade Federal do Paraná, Centro Politécnico, Curitiba 81531-990, Brazil
[c] Embrapa Florestas, Estrada da Ribeira, Km 111, Colombo 83411-000, Brazil

ARTICLE INFO

Keywords:
High hydrophobicity
SiO_2 nanoparticles
Mechanical stability
Time-dependent stability
Wood-based panel

ABSTRACT

We proposed a simple and useful one-step spray coating method to protect MDF panels against physical and mechanical damages commonly presented in indoor real-life conditions. Highly hydrophobic surfaces were designed by TMCS (trimethylchlorosilane)-SiO_2 nanoparticles deposition on MDF panels as a function of concentration of solution (0.1 and 0.3%) and number of cycles (10, 20 and 30 times). The formation of TMCS-SiO_2 coating on MDF surface was investigated by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), X-ray photoelectron spectroscopy (XPS), attenuated total reflectance with Fourier transform infrared spectroscopy (ATR-FTIR) and time-dependent apparent contact angle (WCA). Water drop impacting, dust impacting, and tape-peeling tests were conducted to simulate real-condition damages on MDF surfaces and to investigate the durability of highly hydrophobic coating. The coated MDF panels showed apparent water contact angle exceeding 140° with an interesting time-dependent stability and ability to roll-off, especially because the hydrophobicity of TMCS and hierarchical structure self-organized by spherical SiO_2 nanoparticles. This rougher surface and presence of alkyl groups provide physical and mechanical durability of MDF panels even after water drop and dust impact tests, and tape-peeling up to five cycles. Therefore, this facile one-step MDF coating can be an effective, stable and mechanically durable alternative to protect MDF in undesirable real-life conditions.

1. Introduction

Wood and wood-based products usually have critical limitations to contact with polar liquids due to their high hygroscopicity levels. Although medium density fiberboard (MDF) panels are extensively applied indoors, such as for furniture and cabinet [1,2], some sites like kitchens and bathrooms can lead to an exposure of MDF to undesirable conditions, especially high moisture and direct contact with water.

Many attempts have been explored to fabricate low-energy surfaces -mimicking the lotus effect – to protect wood and wood-based products, such as sol-gel [3,4], dip coating [5,6] and plasma deposition [7–9]. They are based on obtaining low-energy surfaces by contribution of higher surface roughness [10] to improve properties like self-cleanability, mechanical resistance, and UV resistance. These common methods to create a surface with high water repellency are sophisticated and may use several steps and long-times during the chemical reactions. In case of MDF panels, exposure to many chemicals or weathering and long-time reactions may be disadvantageous due to the possible negative chemical interaction with the main components of this material, especially wood fibers and urea-formaldehyde resin. For example: exposure to sunlight irradiation can degrade chemical structure of MDF surface; and aqueous solutions applied for long time to coat solid wood [11] probably will swell the MDF panels. This complex interaction with polar liquids limits the alternatives to change the MDF surface properties.

Otherwise, spray coating has been used to create highly/super-hydrophobic surfaces in materials from different sources. Superhydrophobic leather was fabricated by coating of polyacrylate emulsion and hydrophobic silica nanoparticles [12], durable superamphiphobic coatings of polyperfluoroalkylsilane-modified multiwalled carbon nanotubes were fabricated on glass slides [13]; self-healing and superhydrophobic solid wood was designed using waterborne perfluoroalkyl methacrylic copolymer (PMC) emulsion mixed with TiO_2 nanoparticles [14] and superhydrophobic metal mesh was produced via reaction of metal salts and alkanethiols [15]. The main reasons to adopt this method are its simple and easy procedure, time-saving process, and commercial availability [12,15]. Furthermore, it allows future repairs in case of mechanical

* Corresponding author at: Washington Luiz Esteves Magalhães - Embrapa Florestas, Estrada da Ribeira, Km 111, Colombo 83411-000, Brazil.
E-mail addresses: pedroc@ufpr.br (P.H.G.d. Cademartori), wido@fisica.ufpr.br (W.H. Schreiner), washington.magalhaes@embrapa.br (W.L.E. Magalhães).

https://doi.org/10.1016/j.porgcoat.2018.08.032
Received 12 March 2018; Received in revised form 24 August 2018; Accepted 31 August 2018

damages like exposure of parts of the raw material when in service.

In addition, most of the studies involving surface modification of lignocellulosic materials by micro/nano particles like SiO_2, TiO_2 and Al_2O_3 were performed mainly on natural fibers, paper, and solid wood [5,14,16–18]. Only few studies demonstrated the behavior of wood-based panels coated with micro/nano particles to achieve water-repellent surfaces, such as silver deposition on MDF [19] and polyester powder based on iso- and teraphthalic acid plasma deposition on MDF [20]. Thus, the question how MDF panels will behave with these micro/nanometric coatings is not fully answered. In the knowledge of wide indoor applications of MDF panels and its negative interaction with polar liquids simpler and useful methods can be designed for protection and prevention of MDF surfaces. In our study, we reported a facile one-step spray coating of TMCS-SiO_2 nanoparticles to fabricate highly hydrophobic MDF surfaces. This method did not require complex procedure and supports partial recovery of the surfaces in case of mechanical damages when applied in real-life conditions. The best conditions to create a highly hydrophobic surface were investigated by morphological, physical, and chemical techniques. Practical tests like drop impacting and dust impacting were performed in the highest water-repellent MDF panels to determine physical and mechanical durability.

2. Material and methods

2.1. Materials

Fumed SiO_2 powder (S5130, particle size 0.007 µm), trimethylchlorosilane (TMCS, ≥98%) toluene (anhydrous, 99.8%) and isopropanol (anhydrous, ≥99.5%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethanol (technical grade, 99%) was purchased from Vetec Quimica Fina Ltda (Duque de Caxias, RJ, Brazil). All the chemicals were used as received. Commercial MDF panels made with *Pinus spp* fibers and urea-formaldehyde resin were supplied from the local market of Curitiba, Southern Brazil. The panels were cut in small samples of 25 × 25 x 18 mm (length x width x thickness).

2.2. Functionalization of silica nanoparticles

Fumed SiO_2 nanoparticles (1 g) and 30 mL of toluene were put in a flat-bottom flask. After adding 2 mL of TMCS, they are refluxed for 24 h accompanied by vigorous agitation. This step was carried out in an environment with low humidity due to the high reactivity of TMCS with hydroxyl groups. Then, the reacted material was centrifuged at 5000 rpm for 10 min, followed by sequential washing with toluene (3 times) and ethanol (2 times). The material was dried at 103 °C and a fine reacted SiO_2 powder was obtained.

2.3. Preparation of highly hydrophobic MDF surfaces

Hydrophobic SiO_2 nanoparticles were mixed with isopropanol through ultrasonication for 10 min to obtain solutions with 0.1 and 0.3% (v/v) concentration. Prior to the coating step, the MDF samples were sanded with 100-grit sandpaper to remove the inactive layer from the surface, followed by an air jet for the residual dust. The coating solutions (0.1 and 0.3%) were sprayed on the MDF surface and oven-dried at 60 °C for 5 min. This spray-coating was repeated for 10, 20 and 30 cycles for both solutions. Finally, coated MDF samples were kept in an oven at 60 °C for 24 h to evaporate the solvent and moisture.

2.4. Characterization

The surface morphology of untreated and coated MDF samples were characterized using a scanning electron microscopy (SEM, VEGA3, TESCAN, Czech Republic) at accelerating voltage of 10 kV. An Energy Dispersive X-ray Spectroscopy (EDX) apparatus coupled to SEM was used for the elemental chemical analysis.

Changes on surface chemistry of MDF were investigated by X-ray photoelectron spectroscopy (XPS, VG Microtech ESCA 3000, England). General survey and high-resolution spectra (C 1s) were recorded using Mg Kα radiation with photo energy at 1253.6 eV. The C1s peak (285 eV) was used as reference to compensate the surface charging effects. Attenuated total reflectance with Fourier transform infrared (ATR-FTIR) spectra were collected on a Vertex 70 spectrometer (Bruker Corporation, Billerica, Massachusetts, USA). The equipment was set for measurements at resolution of 4 cm^{-1} and 32 scans in a range of 600–4000 cm^{-1}. Spectra were normalized in the range spanning from 0 to 1 to reduce external effects in the same order of magnitude and to eliminate differences due to possible concentration variations [21–23].

The apparent contact angle (WCA) was determined in a goniometer KrüssDSA25 (Krüss GmbH, Germany) using the sessile drop type contact angle technique. Three droplets of distilled water (surface tension of 72.80 $mN\,m^{-1}$) with 5 µl volume were deposited on surface of untreated and coated MDF samples for 60 s. The time-dependent WCA was determined over 60 s to investigate hydrophobic stability of the surface.

Water drop impacting test was performed by spreading 200, 400 and 1000 mL of distilled water at 0.3–0.5 mL/s on the coated MDF surface. The samples remained 2 h in an oven at 60 °C to evaporate residual water from the surface. Natural sand was collected, homogenized with a mortar and pestle and only particles with granulometry ≤600 µm was selected to the dust impacting test. Two-hundred grams of sand were spread on the coated MDF surface at 60 mm of distance and rate of 8.7 g/s. The spreading process was repeated 5 times for each sample. Tape-peeling test was conducted by applying tape Scotch 810 on the coated MDF surface for up to 50 times. Changes on the surface properties after the durability tests are monitored through WCA measurements.

3. Results and discussion

3.1. Surface morphology

Fig. 1 illustrates morphological changes after coating with hydrophobic SiO_2 nanoparticles on MDF surface. Untreated MDF is represented by tangled fibers with a roughened surface. Deposition of hydrophobic SiO_2 nanoparticles increased the surface roughness due to the presence of nanoscale particulate protrusions. This increase of roughness is driven by the particles size and its voids space created on the surface [24]. Although the nanoparticles are scattered over the fibers' surface treated with 30 cycles and 0.1% hydrophobic SiO_2 concentration, highly magnification images reveal partial agglomeration of the nanoparticles. Another interesting characteristic is lower hydrophobic SiO_2 concentration (0.1%) is not enough to cover the entire surface with a continuous film, since the fibers are partially exposed.

The amount of hydrophobic silica on the MDF surface was adjusted by the spray-coating cycles and solvent concentration. Increasing the hydrophobic SiO_2 concentration with higher number of cycles sprayed on the MDF surface resulted in a continuous film over the MDF covering the entire surface. The interaction with water is one of the most critical problems found in MDF since this results in higher swelling of the material. Covering the entire surface, tangled fibers of MDF remain unexposed on the surface, avoiding the contact with polar liquids. Highly magnification images characterized this film as an intense agglomeration of nanoscale hydrophobic SiO_2 particles, resulting in MDF with lower surface energy. The significantly presence of silica on the MDF surface is confirmed by EDS (see Supplementary material - EDS) with ~3% and ~28% for 0.1% and 0.3% hydrophobic SiO_2 concentration, respectively. Cracking observed in the coating is probably due to the drying stress during the step of evaporation of isopropanol.

3.2. Chemical composition

Based on the XPS spectra, the atomic concentration of carbon, oxygen and silicon, and the Si/C and O/C atomic ratios were