

FABRICATION OF SUPERHYDROPHOBIC
WOOD SURFACE
WITH A SILICA/SILICONE OIL COMPLEX EMULSION

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ABSTRACT

The superhydrophobic wood surface was fabricated in this study by impregnating oven-dry poplar (*Populus cathayana* Rehd.) samples with a silica/silicone oil complex emulsion (SSOCE), mainly composed of two silicone oils (hydroxy silicone oil and hydrogen silicone oil) and two different sized silica particles (micron and nano scaled, respectively). Different concentrations of the complex emulsion (5%, 10%, 20%, 30% and 40%) were used and their effect on static contact angles (CAs) and surface free energy (SFE) of wood were investigated. The chemical and morphological changes of modified wood surface were characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS). The superhydrophobic wood surfaces were manifested by the water CA of about 154.8° on the transverse section, 151.3° on the tangential section and 150.2° on the radial section, respectively. It was confirmed that silicone oils in the complex emulsion formed a silicon resin film and uniformly attached on the wood surface, with silica particles in micron and nano scales helped to make the surface rougher.

KEYWORDS: Wood, silicone oil emulsion, silica particle, superhydrophobicity, contact angle.

INTRODUCTION

Recently, many botanists focused their research on the microrelief of plant leaf surfaces, and found that epicuticular wax crystalloids and surface roughness are the main causes for self-cleaning and water repellent mechanism of many biological surfaces. For example, the lotus leaf is highly water-repellent with a contact angle above 150° and a rolling angle below 10° , so the particles on it can be removed completely by water droplets that roll off the surfaces, independent of their chemical nature and size of surface roughness. This effect is called the "Lotus-Effect", which has attracted significant attention in academic research, industrial applications and daily life uses over the last two decades (Satoshi et al.1996, Barthlott et al. 1997, Abraham 2004, McHale et al. 2005, Zhang et al. 2013, Wang et al. 2015).

The fabrication of artificial superhydrophobic surfaces on wood has aroused a considerable amount of interest from academia (Liu et al. 2011a, Fu et al. 2012, Kavalenka et al. 2014, Chu et al. 2015, Jin et al. 2015). Various techniques have been used such as the self-assembly method (Lu et al. 2013, Jin et al. 2014), hydrothermal method (Sun et al. 2011, Fuet al. 2012, Gan et al. 2015, Liu et al. 2015), chemical reaction and deposition method (Jin et al. 2015), and sol-gel method (Donath et al. 2004, Wang et al. 2011, Wang et al. 2013, Lu et al. 2013, Gao et al. 2015). However, some treatment procedures and requirements(involved harsh conditions, expensive and harmful compounds, specialized reagents and equipment, etc.) appeared to be too complicated to be feasible in practice.

A wide variety of organo-silicon compounds has been studied for application on wood. Some organo-functional silanes such as 3,3,3-trifluoropropyltrimethoxysilane (TFPTMOS) were combined with tetraalkoxysilanes (TEOS) to impregnate wood in one step (Mai and Militz 2004). However, various physical and chemical factors (e.g. temperature, pH value of the catalyst, $H_2O:Si$ ratio) cause variation in the process of hydrolysis and condensation, as well as in the structure of the obtained products. Hydrolysis and condensation reaction never reach completion even if an excess of water was available so that a polysilicate mixture of intermediate species was formed (Donath et al.2004). Therefore, the reaction conditions were complex, the quality of modified wood was difficult to be controlled and the time required for the experiment was relatively long.

Silicone oils were widely applied in industrial products due to their unique properties of high lubricity, non-toxicity, extensive spreading, and stable film formation (Clarson et al. 2007). Silicone oils as an organo-silicon compound were important water repellents that impart hydrophobicity to wood products (Mai and Militz 2004, Jusoh et al. 2005). The most commonly used silicones were polydimethylsiloxanes (PDMS), which may have side groups of various functionalities (Oliver et al. 2007). Depending on the functionalisation of the silicone oils, the degree of hydrophobicity can vary. Primary hydroxyl group and hydrogenous group as part of a side group increase the affinity of silicone molecules to cellulosic material. The silicone oils, which were developed for application in the textile industry, were usually applied in aqueous systems in the form of macro- or micro-emulsions. The droplet size in these emulsions has significant influence on the liquid penetration into wood matrix. The localization of silicone systems in wood and their influence on water uptake and dimensional stabilization are described in recent studies (Ren et al. 1995, Mai and Militz 2004, Weigen et al. 2007, Vetter et al. 2010). Amongst the various techniques used for the fabrication of a super-repellent surface, coating substrates with silica nanoparticles (SNP) was a widely-used one (Rao et al. 2003, Hsieh et al. 2009, Hsieh et al. 2011, Liu et al. 2011b). The nanosilica particles impart roughness to substrate surfaces, which makes a hydrophobic surface become more hydrophobic, or even superhydrophobic.

Here, we developed a complex emulsion system and used it to fabricate a superhydrophobic surface inside wood after a suitable drying process. Compared with the traditional approaches such as the sol-gel method, this method is simpler and the procedure is more convenient to operate for ensuring the quality of modified wood. In this study, the static contact angles (CAs) and surface free energy (SFE) of the control and modified samples were investigated, and the chemical and morphological alterations of the wood surface were characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), field emission scanning electron microscope (FESEM) and X-ray photoelectron spectroscopy (XPS).

MATERIAL AND METHODS

Materials

Poplar (*Populus cathayana* Rehd.) sapwood samples collected from the northeast of China with an air-dry density of 0.382 g cm^{-3} and an average growth ring width of 0.35 cm were used in this study. The sizes of the samples are $20 \text{ (L)} \times 20 \text{ (T)} \times 20 \text{ (R)} \text{ mm}$ for testing WPG, bulking effect and sorption behavior, $10 \text{ (L)} \times 20 \text{ (T)} \times 20 \text{ (R)} \text{ mm}$ for ATR-FTIR characterization, $5 \text{ (L)} \times 5 \text{ (T)} \times 2 \text{ (R)} \text{ mm}$ for XPS tests, and $3 \text{ (L)} \times 3 \text{ (T)} \times 3 \text{ (R)} \text{ mm}$ for AFM analyses. Prior to the treatment, the wood samples were oven-dried at 103°C to constant mass m_1 (g), and then stored in a climate chamber (20°C , 65% R.H.).

Tab.1: The composition of silica/silicone oil complex emulsion.

Ingredients	Phase	Provided parameters	Content (%)	Provider
Hydroxy silicone oil	liquid	Hydroxyl content 8%	30	Beijing Hang Ping silicone factory, Beijing, China
Hydrogen silicone oil	liquid	Active hydrogen content 1.6%	10	
Hydrophobic silica modified by chloro- silane	powder	Average particle size: 16 nm pH in water: 3.6-4.4	8	AEROSIL R972, Degussa, Germany
Hydrophobic Silica by chloro-silane	powder	Average particle size: $5.5 \mu\text{m}$ pH in water: 5.2-6.0	1	Nanjing Tianshi experiment powder Co., Ltd., China
Emulsifier	liquid	Anionic	5	
Distilled water	liquid	-	46	

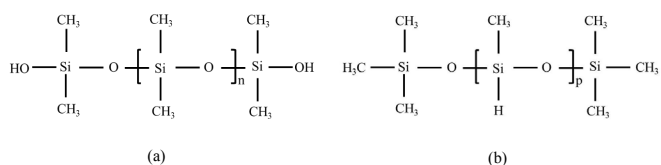


Fig. 1: The chemical structural formula of hydroxy silicone oil (a) and hydrogen silicone oil (b).

The SSOCE used in this study was prepared in laboratory. Its composition is shown in Tab. 1. The hydrophobic nano-silica (AEROSIL R972) was a product of Degussa company of

Germany, which was made by gas phase method. The hydrophobic micro-silica was made in China by a chemical precipitation method. Their average particle sizes are 16 nm and 5.5 μm , respectively. The silicone oils used in the formulation are hydroxy silicone oil and hydrogen silicone oil, with chemical structural formula shown in Fig. 1.

Methods

Preparation of SSOCE

At room temperature, certain amounts of hydroxyl silicone oil, hydrogen silicone oil, anionic surfactant, nano silica, micron silica were put in the 1000 ml beaker according to the formulation listed in Tab. 1, mixed at a speed of 10000 rpm for 10 min by high speed agitator, with successive addition of water, and then ultrasonic treated for another 10 min, to obtain the initial emulsion. Then, the initial emulsion was homogenized at 40 bar by using a high pressure homogenizer to obtain the SSOCE with a solid content of 43 %.

Determination of the particle size of SSOCE

The prepared complex emulsion above was diluted 100 times and a droplet of 3 ml was used to test the particle size distribution by laser particle analyser (Beckman Coulter, USA). The average particle size of the SSOCE was 262 nm, as shown in Fig. 2.

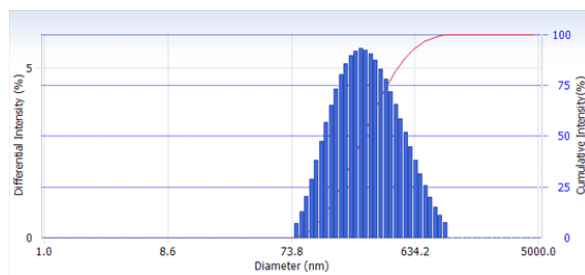


Fig. 2: The particle size distribution of silica/silicone oil complex emulsion (SSOCE).

Modification of wood with SSOCE

Prior to the impregnation procedure, SSOCE was diluted with distilled water to several concentrations (5, 10, 20, 30, and 40% w.t.). The diluted SSOCE was first mixed with zinc acetate as catalyst in a certain proportion and then impregnated into wood via a full cell process. The process included a vacuum of 0.01 MPa for 1 h and a subsequent pressure of 0.5 MPa for 1 h. After impregnation, the samples were weighed and subsequently dried in an oven according to the following schedule: 60°C for 12 h, elevated to 80°C and kept for 12 h, elevated to 103°C and then dried to constant mass m_2 (g). The weight percent gains (WPGs) of the treated samples were calculated according to Eq. 1, based on the data of six replicates. And then the samples were sealed in plastic bags and cooled down.

$$\text{WPG} = \frac{m_2 - m_1}{m_1} \times 100 \quad (\%) \quad (1)$$

CA and SFE characterization

The CAs of three reference liquids (water, formamide, and diiodomethane) on the sample surfaces (transverse, radial, and tangential) were measured by the sessile drop method on a contact angle analyzer (OCA20, DataPhysics Instruments GmbH, Filderstadt, Germany). The

contact angle of the untreated wood sample surface used the initial contact angle due to the fast penetration of water, while the contact angles of SSOCE treated sample surfaces were determined after the water droplet has contacted the wood surface for 5s. For each test, 2 μL liquid was used to form the droplet. The average value of 5 replicates were taken as the final contact angle, but if the deviation of the 5 measurements was too large, then the average value of 10 measurements was used. Surface free energy of unmodified and modified wood samples were calculated by software of contact angle analyzer, according to the Lifshitz-van der Waals acid-base theory (Van Oss 2002, Wang et al. 2015). The total surface free energy is a sum of the apolar (Lifshitz-van der Waals, γ^{LW}) and polar (Lewis acid-base, γ^{AB}) parts. γ^{AB} can be expressed in terms of electron-accepting component (γ^+) and electron-donating component (γ^-) (Wang et al. 2015).

ATR-FTIR analyses

Spectra of wood sample surfaces, hydroxysilicone oil, hydrogen silicone oil and silicon resin film were recorded by an ATR-FTIR spectrophotometer (Vertex 70v, Bruker Corporation, Germany) in a transmission mode within the range of (4000-600) cm^{-1} .

XPS analyses

The surface chemical elements of untreated and SSOCE treated samples were analyzed by XPS (Escalab 250Xi, Thermo Scientific Company, America) with an acceleration voltage of 13 kV and nonmonochromatic $\text{MgK}\alpha$ and $\text{AlK}\alpha$ X-radiations ($h\nu=1253.7\text{eV}$ and 1486.7eV , respectively). The samples were analyzed in vacuum ranging from 1.33×10^{-6} to $1.33\times 10^{-5}\text{Pa}$. The survey scans were collected from the binding energy range of 0 to 1350 eV.

AFM analyses

A small cubic sample with a size of 3(T) \times 3 (R) \times 2(L) mm cut from 40 % SSOCE treated wood was first fixed on the work bench and then its transverse section was observed with AFM.

RESULTS AND DISCUSSION

Weight percent gains (WPGs)

The average WPGs of the wood samples treated with 5%, 10%, 20%, 30%, 40% concentrations of SSOCE were respectively 2.16%, 4.53%, 10.90%, 16.27%, and 19.83%. With the increasing concentration, WPG increased accordingly, which suggests that the emulsion could penetrate into wood successfully.

Surface hydrophobicity

The surface hydrophobicity of untreated and SSOCE treated wood samples was investigated through determination of water contact angles (WCA) and determination of the surface free energy (SFE). The WCAs are plotted in Fig. 3. The average WCAs on three sections of control samples were respectively 102.6° (transverse), 95.6° (tangential) and 96° (radial). After SSOCE treatment, the WCA significantly increased. For 5% SSOCE treated wood surface, the WCAs were elevated to 154.8° (transverse), 151.3° (tangential) and 150.2° (radial), denoting the formation of superhydrophobic wood surfaces. The WCA of the cross section was slightly higher than the WCAs of other two surfaces, which might be related to different surface structures of the three surfaces and the difference on surface roughness after treatment (Hsieh et al. 2005). With the increasing concentration of SSOCE treatment, WCAs on all three wood surfaces

showed a decreasing trend. It might be caused by the reduced surface roughness at thicker coated surface. The surface roughness is considered a primary factor influencing the wood surface hydrophobicity (Bhusha et al. 2007, Hsieh et al. 2008).

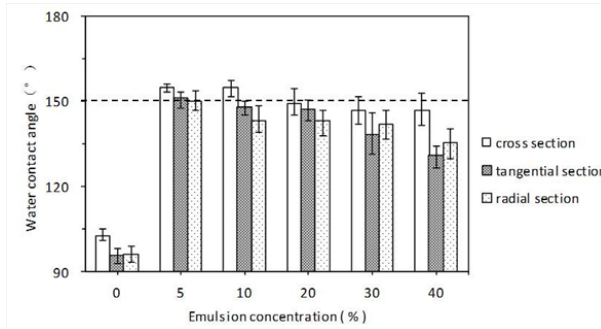


Fig. 3: Water contact angles (WCAs) on surfaces of wood samples, untreated or treated with different concentrations of silica/silicone oil complex emulsion.

According to the Lifshitz-van der Waals acid-base theory, the SFE of untreated control and treated sample surfaces were calculated and listed in Tab. 2. All concentrations of SSOCE treatments could reduce the surface free energy on either transverse, radial or tangential surface, namely, the hydrophobicity of wood surface was improved after treatment. The transverse wood surface treated with 5% SSOCE showed the lowest SFE ($8.34 \text{ mJ}\cdot\text{m}^{-2}$), which is consistent with the WCA trend. We also tested the SFE value of dried lotus surface, its SFE value is extremely low with a γ^{LW} of $1.06 \text{ mJ}\cdot\text{m}^{-2}$ and a γ^{AB} of zero. The SFE values vary somehow on three surfaces, which was considered to be attributed to difference in wood extractive composition and the diversities in anatomical features in these directions (Nussbaum 1989).

Tab. 2: Surface free energy of the wood samples treated by different concentrations of silica/silicone oil emulsion based on the Lifshitz-van der Waals acid-base theory.

SSOCE concentration (%)	Surface free energy ($\text{mJ}\cdot\text{m}^{-2}$)		
	Cross section	Tangential section	Radial section
0	48.30	46.32	42.38
5	8.34	11.10	14.56
10	9.90	15.00	22.32
20	15.56	17.17	23.57
30	19.77	17.94	24.53
40	23.61	24.57	28.50

Surface chemistry analyses

In order to investigate the interaction between SSOCE and wood, both silicone oils, the formed silicone resin film, and also the untreated and treated wood surfaces were investigated by ART-FTIR. The results are shown in Figs. 4 and 5. Silicone oils contain Si-O-Si, Si-O, and freely rotating methyl groups (CH_3 -), rendering them hydrophobicity (Somasundaran et al. 2006). In Fig. 4, the absorption bands at 1024 cm^{-1} (hydroxy silicone oil), 1043 cm^{-1} (hydrogen silicone oil), 1016 cm^{-1} (silicon resin film) are all assigned to Si-O-Si bonds (Lai et al. 2013,

Wanget al. 2013, Chu et al. 2015). The absorption peaks at 1260 cm^{-1} , 795 cm^{-1} , 764 cm^{-1} , 792 cm^{-1} are assigned to Si-CH₃ bond (Lai et al. 2013, Chu et al. 2015), and the absorption peaks at 2964 cm^{-1} are corresponding to C-H bond in Si-CH₃ bond. As the characteristic bands in both silicone oils, Si-OH bond denoted by 3304 cm^{-1} and 891 cm^{-1} bands and Si-H bond denoted by 2168 cm^{-1} and 808 cm^{-1} bands can also be observed (Lai et al. 2013, Chu et al. 2015). In silicon resin film, the Si-OH bond disappeared but Si-H bond still showed a small band, suggesting the existence of a small amount of unreacted hydroxy silicone oil.

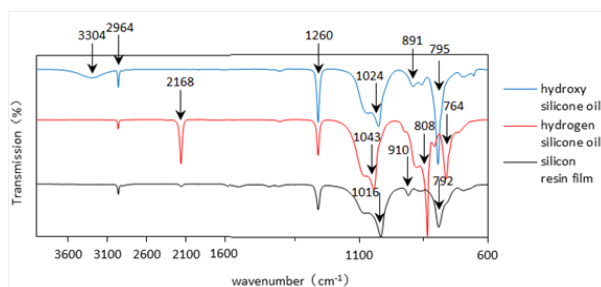


Fig. 4: ATR-FTIR spectra of hydroxy silicone oil, hydrogen silicone oil and silicon resin film.

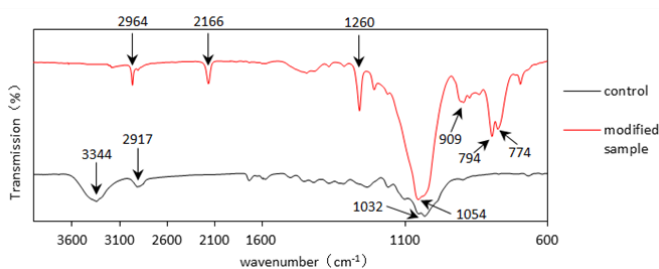


Fig. 5: ATR-FTIR spectra of untreated control and SSOCE treated wood surfaces.

In Fig. 5, the ATR-FTIR spectra of untreated control and SSOCE treated wood surfaces are compared. For untreated control, the absorption bands at 3344 cm^{-1} , 2917 cm^{-1} and 1032 cm^{-1} are assigned to the stretching vibration of O-H bond, the asymmetric and symmetric stretching of C-H (CH₃ and CH₂) bond and the stretching vibration of C-OH bond (Lai et al. 2013, Wang et al. 2013). While for SSOCE treated wood, the absorption band for O-H disappeared, while some new absorption bands emerged, such as the bands at 2964 cm^{-1} (assigned to C-H in Si-CH₃), 1260 cm^{-1} and 794 cm^{-1} (assigned to Si-CH₃), 1054 cm^{-1} (assigned to Si-O-Si bond), suggesting that hydrophobic silicon resin film had been formed on the surface of the SSOCE treated wood surface. However, there is a new absorption band for Si-O, Si-C or Si-O-C Si-O-C (774 cm^{-1}) bond in Fig. 5, suggesting that the combination between wood surface and silicone resin film might depend on covalent bonding (Tshabalala et al. 2003, Li et al. 2008, Wang et al. 2013). The two kinds of silicone oils first react with each other with the help of a catalyst, then the silanol groups from the hydrolysis of the alkoxy groups insilanes react with the hydroxyl groups of cell wall polymers, and finally form a covalent bond between them (Donath et al. 2004).

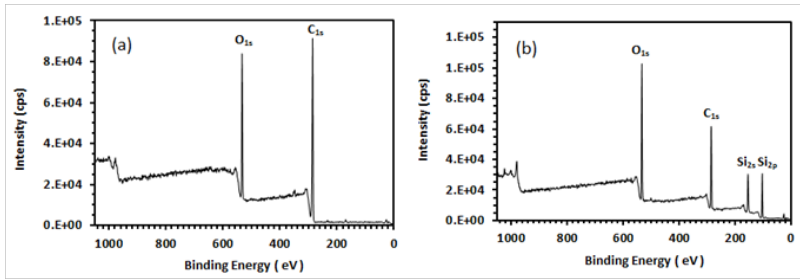


Fig. 6: XPS spectra of untreated control (a) and SSOCE treated (b) wood surface.

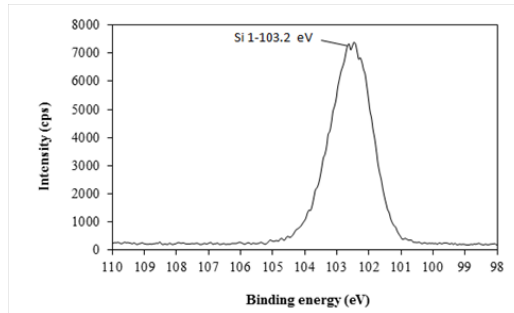


Fig. 7: Si_{2p} high-resolution XPS spectrum of modified sample surface with silicone oils emulsion.

The surface chemistry changes after treatment were also characterized by XPS. As compared to untreated control (Fig. 6a), the relative intensity of C and O peaks changed significantly, and Si_{2s} and Si_{2p} peaks resulted from the deposition of silicone resin film on wood surface appeared (Fig. 6b).

The value of the binding energy (103.2 eV) of the Si component of the Si_{2p} peak is consistent with the presence of a silicon atom linked to an oxygen atom as in Si-O-C in Fig. 7, it also indicated that the combination between wood surface and silicone resin film might depend on covalent bond (Si-O-C) (Tshabalala et al. 2003).

Surface morphology analyses

The surface morphology of SSOCE treated wood was investigated by AFM. The results are shown in Fig. 8. For the surface of transverse section, it can be found that the surfaces were very rough, with protrusions of micron or nano scales on a continuous film. During the successive drying process after impregnation, the demulsification of SSOCE occurred in both outer surface and inner surface of treated wood with the evaporation of the water. Meanwhile, silicon resin film containing both silica and silicone oils was formed with the help of catalyst. In this study, two sizes of silica particles were used. Therefore, the protrusions should be attributed to these silica particles, and the resin film was mainly formed by the silicone oils, which together constitute a rough wood surface. The design of such a dual-size roughened surface was aimed to mimic the surface of a lotus leaf.

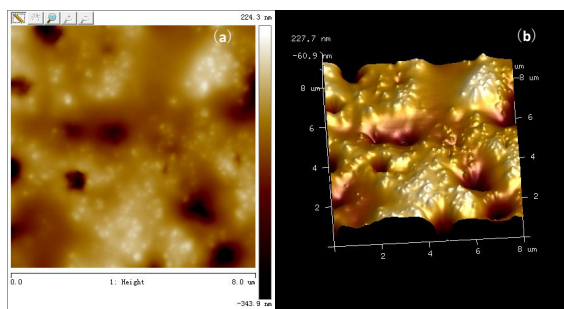


Fig. 8: AFM micrographs of SSOCE treated wood surfaces of transverse section. (a) 2D image, (b) 3D image.

CONCLUSIONS

The silica/silicone oil complex emulsion used in this study can fabricate superhydrophobic surfaces on or in wood. A suitable concentration (5% in this study) can increase the water contact angle to above 150 degrees on all three wood surfaces and reduce the surface free energy to a very low level. This is because a continuous silicon resin film has been formed on the outer surface or on the surface of wood cell wall, which forms covalent bond Si-O-C with wood polymers. Also, the dual-sized silica particles formed nonregular protrusions in the resin film, which helped to form a rough surface and improved the hydrophobicity as mimicking the surface structure of lotus leaf. Further study would be focused on optimizing the constituents of the complex emulsion and investigating the effect of this treatment on other wood properties.

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