ORIGINAL RESEARCH

Wood protective coatings based on fluorocarbosilane

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Abstract The effectiveness of protective coatings based on 3-(2,2,3,3,4,4,5,5-octafluoropentyloxy)propyltriethoxysilane in the protection of wood surface from the effects of water was tested. No earlier attempts at using the mentioned fluorocarbosilane for the protection of wood have been reported in the literature. The coatings were deposited by the sol–gel method. As a result of the generation of chemical bonds between the wood surface and silane, a coating was produced that permanently increased the wood hydrophobicity. Fluorinated chains attached to the silicon atoms make an effective barrier preventing the access of water and limiting the effects of water on the wood surface.

Keywords Fluorocarbosilane · Sol–gel processes · Wood protection

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Introduction

Wood is one of the most important construction materials. Unfortunately, it undergoes a steady, slow process of deterioration when exposed to the natural elements such as water, oxygen and irradiation, so it must be protected against their influence. The appropriately chosen method of wood protection increases its durability and extends the time of its use, thus reducing the cost of maintenance (Goodell et al. 2003). A number of methods have been proposed for wood protection, based on its chemical modification (Marney and Russell 2008; Naumann et al. 2012) and surface treatment (Subasri et al. 2013).

Many of the hitherto used wood protection agents are highly toxic for humans, so recently much attention has been paid to design non-toxic wood-protecting materials or methods. Quite recently a few papers on the use of inorganic–organic hybrid coatings for wood surface protection have been published (Mai and Militz 2004b; Tshabalala and Gangstad 2003; Tshabalala and Sung 2007). The sol–gel process is widely applied for the production of hybrid coatings. The inorganic–organic coatings obtained by this method can be deposited at room temperature on a wide range of surfaces, including wood.

Fluorine-containing organosilicon derivatives have recently attracted much interest because of the possibility of their use for the manufacture of modern materials. Fluoroalkylsilanes are used as surfactants,

as agents for the modification of lenses and fiber optic cables, as components of many cosmetic preparations and as modifiers of fluorinated polymers and silicon rubbers. Particularly attractive is their use in the production of surfaces resistant to oil, dirt and water (Bukowski et al. 2005; Dopierala et al. 2013; Iacono et al. 2007; Riess and Krafft 1998; Wong et al. 2003). The unique properties of perfluorinated silicon compounds, in particular low surface energy that stems from the presence of fluoroalkyl groups, are very attractive from the point of view of their application for producing wood protective coatings. Unfortunately, the limited access to substrates and complicated synthesis restrict the use of fluoroalkylsilanes in wood surface coatings (Chen et al. 2017; Lu and Hu 2016; Wang et al. 2011).

In this paper we would like to present the wood protecting effects of fluorocarbosilane (3-(2,2,3,3,4,4,5,5-octafluoropentyloxy)propyltriethoxysilane, OFTES) coatings that have not been reported earlier. Our experience in the area permitted designing and synthesizing fluorinated derivatives of organofunctional silanes (Karasiewicz et al. 2014). The wood-protecting properties of the coatings made of these materials have been studied by a number of methods for surface analysis and water absorption tests.

Experimental

Materials

Pine wood boards, purchased from the lumber mill, were cut into smaller pieces of dimensions 70 mm × 20 mm × 10 mm (longitudinal × tangential × radial, respectively). All reagents were purchased from Sigma Aldrich, except ethanol and acetic acid (Avantor Performance Materials, Poland). 3-(2,2,3,3,4,4,5,5-octafluoropentyloxy)propyltriethoxysilane (OFTES) with the formula $HCF_2(CF_2)_3CH_2O(CH_2)_3Si(OCH_2CH_3)_3$ was synthesized according to the procedure described in the literature (Karasiewicz et al. 2014). All chemicals were used as received without further purification.

Modification of wood surface by the treatment with silane OFTES

All wood samples were ultrasonically washed for 5 min with acetone, ethanol and deionized water, respectively. Three samples labeled with the letter F were dried without further treatment, while the other three samples labeled as FS were coated with silica nanoparticles, according to the procedure described by (Wang et al. 2011). Then the clean samples (F) and samples with the silica nanoparticles on the wood surface (FS) were dried in an oven at 60 °C for 12 h and directly used for further modifications. After that a series of three 5% solutions of OFTES in ethanol were prepared (Table 1).

The prepared solutions were stirred for 30 min, except for the solutions for the samples F3 and FS3 that were stirred for 72 h. After the stirring, the wood samples were subjected to full submersion in the solutions for 1 h, followed by taking them out and drying in air for 1 h (room temperature, 20% humidity) and in an oven at 60 °C for 12 h.

Analyses and measurements

Scanning electron microscopy (SEM) images were taken using a FEI Quanta 250 FEG microscope equipped with an EDAX Energy Dispersive Spectroscopy detector (EDS). The images of longitudinal wood samples section were taken in high vacuum mode and accelerating voltage of 5 kV. The samples were prepared by gluing the wood onto the standard SEM carbon adhesive tape.

Table 1 Amounts of reagents used for preparation of silane solutions

Symbol	Reagents (g)				
	OFTES	Ethanol	Acetic acid	Water	TEOS*
F1/FS1	5	87	6	2	–
F2/FS2 and F3/FS3	5	59	6	8	22

TEOS tetraethoxysilane

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 Fourier transform spectrometer equipped with a SPECAC Golden Gate diamond ATR (attenuated total reflection) unit. In all cases 16 scans at the resolution of 2 cm^{-1} were collected for a spectrum. For each sample, measurements were made at three sites and the spectra were averaged using the OPUS Data Collection Program.

Static water contact angle (WCA) measurements of all samples were made using a Krüss GmbH DSA 100 Expert Drop Shape Analyzer equipped with a software-controlled (DAS4 2.0): x, y, z-axis table, quadruple dosing unit with zoom and focus adjustment, illumination, and a camera with 780×580 px resolution. All the presented data are arithmetic means of values measured for 5 drops per sample. The measurements of contact angles were performed immediately after the deposition of a drop on the studied surface and the measurement time was about 1 s.

Water absorbability was measured for the wood samples dried at 110 °C to constant mass, weighed to the accuracy of 0.001 g, fully submerged in distilled water for 24 h. Then the samples were taken out, dried with filter paper and weighed again. Percentage of water absorbed was calculated according to the formula:

$$\%M = \frac{M_{wet} - M_{cond}}{M_{cond}} \times 100\%$$

where %M is the percentage of water absorbed (%); M_{wet} the wet mass after submersion in water for 24 h (g); M_{cond} the conditioned mass (initial dry mass) (g). All the obtained coatings were tested on three samples in parallel and the results were averaged.

Results and discussion

Analysis of surface morphology

The silica nanoparticles and all OFTES-based coatings were prepared through a typical sol–gel process. In sol–gel solutions the reactions of hydrolysis and condensation take place (Mai and Militz 2004a; Subasri et al. 2013; Wang et al. 2011). The former reaction leads to the formation of Si–OH groups from water present in the solvent. The condensation of silica nanoparticles proceeded in a basic environment, while the condensation of the OFTES-based coatings proceeded in acetic acid. As a result of the reaction of condensation between Si–OH and Si–O–CH$_2$CH$_3$ groups, a well-developed cross-linked structure with the covalent bonds Si–O–Si was formed. The obtained gel was deposited on the wood surface. The covalent bonds of wood-O–Si were generated as a result of reactions proceeding between –OH groups existing on the wood surface and the Si–OH and Si–O–CH$_2$CH$_3$ groups present in the solvent.

Figure 1 presents the SEM images of a bare pine wood sample (Fig. 1a) and a sample covered with silica nanoparticles (FS0) (Fig. 1b). The image in Fig. 1b clearly shows silica nanoparticles deposited on wood cell walls and filling the furrows in the wood structure. As mentioned earlier, the silica nanoparticles adhere to the wood surface due to formation of chemical bonds between the hydroxyl groups on the wood surface and silica nanoparticles.

Figure 2 shows the EDS spectra of the bare pine wood (Fig. 1a) and of the wood covered with silica nanoparticles (FS0) (Fig. 1b). The spectrum of bare wood displays only signals coming from carbon and oxygen, while the spectrum of the sample FS0 shows an additional signal assigned to silica nanoparticles.

The OFTES-based coatings were deposited on the sample of bare wood and the sample pre-covered with silica nanoparticles. All coatings were analyzed by SEM. The SEM images of all OFTES-covered samples at a higher magnification (Fig. 3) reveal additional layers covering the wood surface. In Fig. 1a showing the unmodified wood, the edges of wood structure are sharp, whereas in Fig. 3a, c and e that show samples covered with OFTES, the edges are blurred. The SEM images of the wood samples precoated with silica nanoparticles, presented in Fig. 3b, d and f, also reveal a partial disappearance of silica spheres because of their partial coverage with an OFTES-based coating. The SEM images of the samples F3 and FS3 (Fig. 3e, f) show additional silica spheres formed from TEOS.

Figure 4 presents the EDS spectra of the wood samples covered with an OFTES-based coating. The presence of signals assigned to silicon atoms and fluorine atoms confirms the formation of an additional organosilicon layer based on OFTES.

Subsequently, all the prepared samples have been subjected to FT-IR analysis which also confirmed successful wood surface functionalization. Due to the
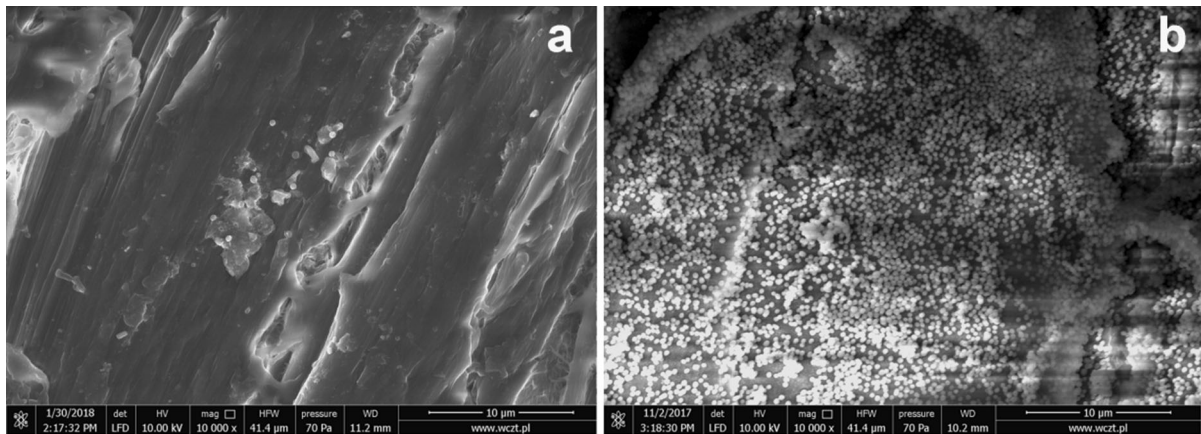
Fig. 1 Scanning electron microscope images: **a** bare pine wood, **b** wood covered with silica nanoparticles (FS0)
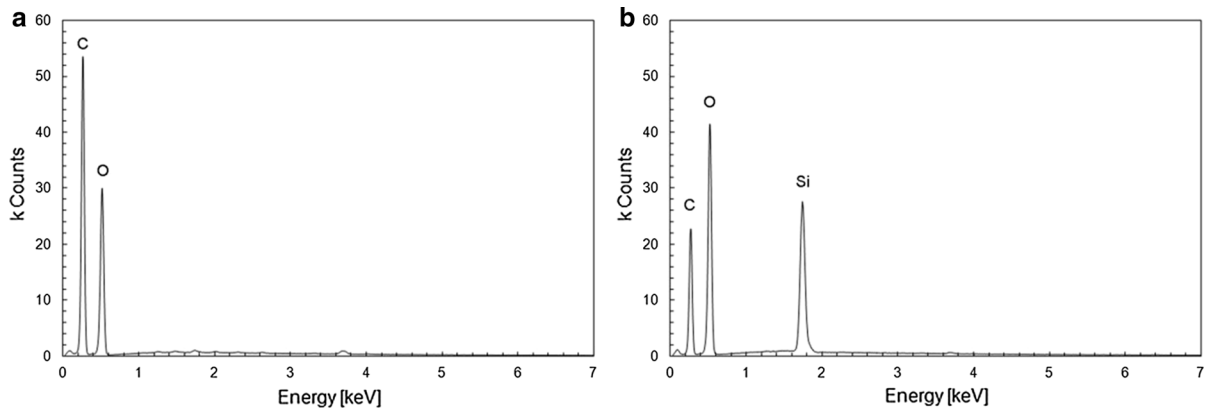

Fig. 2 EDS spectra: **a** bare pine wood, **b** wood covered with silica nanoparticles (FS0)

substantial chemical and physical heterogeneity of the studied samples, that is typical of wood, and relatively low intensities of the collected spectra, each sample was measured in 10 randomly selected points and the obtained spectra were averaged to get a reliable result. Averaged spectra of F1–F3, FS1–FS3 samples are juxtaposed in Fig. 5 together with the spectrum of bare wood sample. The latter spectrum contains only low intensity bands originating from the stretching vibrations of O–H bonds in the range of 3600–3000 cm^{-1} and overlapped bending and scissoring vibrations of ν(C–C), ν(C–O) and ν_s(C–O–C) bonds in the range of 1100–900 cm^{-1} characteristic of cellulose, lignin and hemicellulose (Emmanuel et al. 2015), whereas in the spectra of F1–F3, FS1–FS3 samples several new bands of significantly higher intensities appeared in the ranges of 3600–2800, 1800–1500 and 1300–750 cm^{-1}. A broad band observed in the range from 3600 to 3000 cm^{-1} should be attributed to the presence of the silanol (Si–OH) groups formed as a result of hydrolysis of triethoxysilyl groups of the employed silanes. A new band with the maximum at 2930 cm^{-1}, observed for all coated samples, should be ascribed to the presence of C–H bonds in the alkyl chains of fluorosilane and nonhydrolyzed ethoxy groups. Another broad band present in the spectra of coated samples, that appears in the range of 1300–850 cm^{-1}, is a result of overlapped stretching vibrations of Si–O–Si, C–F and C–O–C bonds and it proves the successful formation of siloxane coating. The formation of Si–O–Si framework on the surface of modified samples is also confirmed by the presence of a broad band originating from stretching vibrations in the range of 1800–1500 cm^{-1} and a low intensity band with the maximum at 830 cm^{-1} that is attributed to the bending vibrations of Si–O–Si bonds.
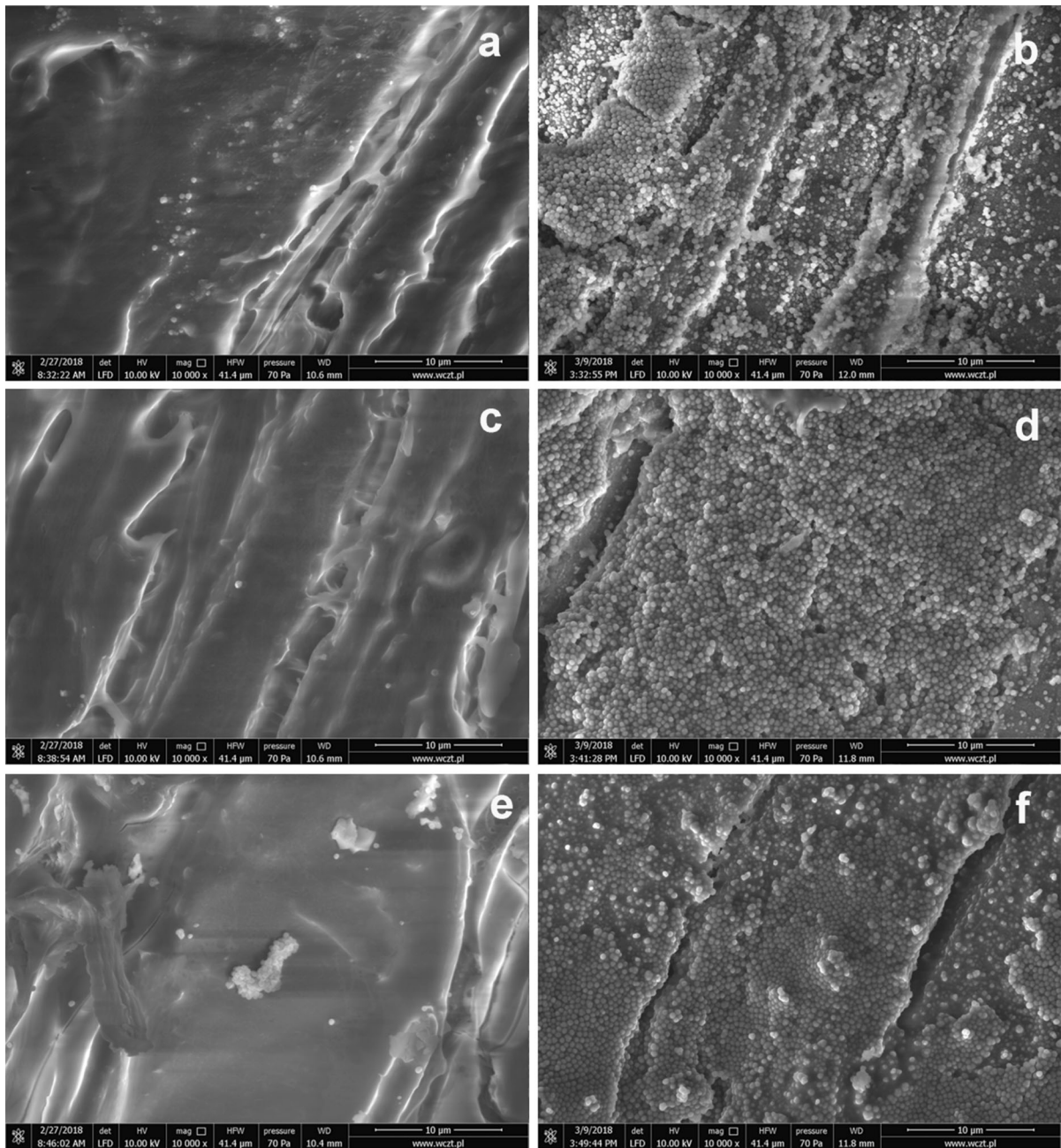
Fig. 3 Scanning electron microscope images of samples: **a** F1, **b** FS1, **c** F2, **d** FS2, **e** F3, **f** FS3

Moreover, important differences in the structure of coatings formed by the single-step (F1–F3) and two-step process (FS1–FS3) can be seen in the collected spectra. Significantly lower area of 3600–3000 cm^{-1} band observed for the FS sample series suggests a higher conversion of Si–OH and the formation of more condensed Si–O–Si framework. The difference in the nature of the formed layers is also revealed in the change of the 1300–850 cm^{-1} band geometry and the shift of its maximum to higher wavenumbers.

Additionally, the values of standard deviations calculated for all the presented spectra (Fig. 6) suggest that the uniformity of the coatings formed from the solution containing higher amount of water and an
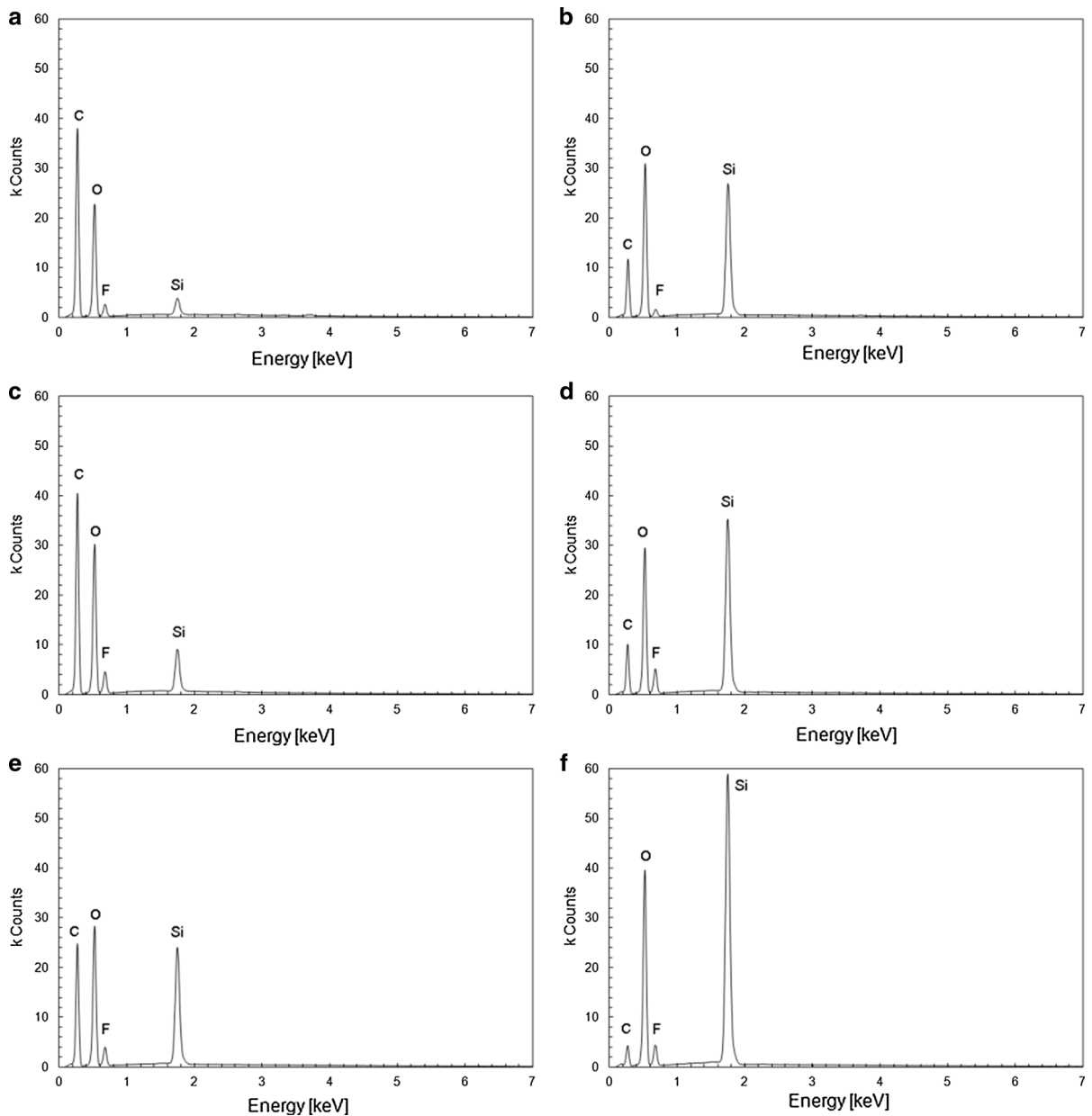
Fig. 4 EDS spectra of the samples: **a** F1, **b** FS1, **c** F2, **d** FS2, **e** F3, **f** FS3

additional amount of tetraethoxysilane (F2 and FS2) is better than that created on the surface of F1 and FS1. This effect is even more pronounced for samples F3 and FS3 which suggests that prolonged hydrolysis of the impregnating solutions promotes the formation of more uniform coatings. It should be noted that the standard deviations calculated for the spectra of FS1–FS3 samples were lower than those for F1–F3 samples which also proves the beneficial effect of the presence

of silica nanoparticles on the coating protective quality.

In Table 2 the water contact angles (WCA) on bare wood and coated wood samples are given. The WCA value on the bare wood surface shows that the latter is hydrophilic since it is characterized by WCA below 90°, while in the case of the wood sample covered with silica nanoparticles it was impossible to measure the water contact angle because the drop of water spread
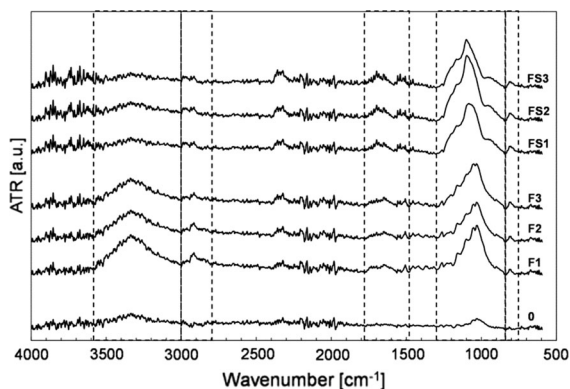
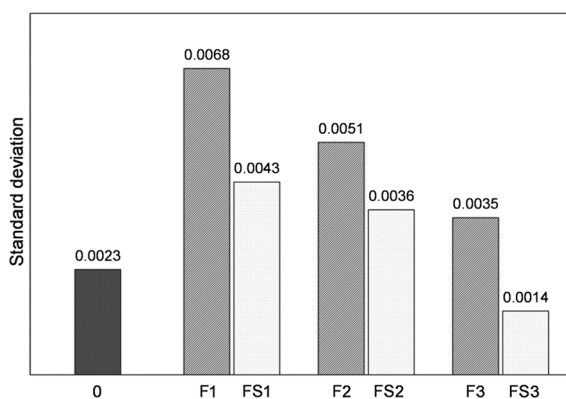**Fig. 5** FT-IR spectra of bare pine wood and all the coated samples

Fig. 6 The chart of standard deviations calculated for the FT-IR spectra

Table 2 Water contact angle (WCA) values of bare wood and coated samples

Sample	WCA (°)
Bare wood (F0)	55.12 ± 3.52
FS0	–
F1	112.54 ± 3.93
F2	105.12 ± 3.20
F3	100.48 ± 3.19
FS1	131.87 ± 3.53
FS2	121.59 ± 2.05
FS3	120.46 ± 6.21

over the surface too quickly. The nature of the OFTES-coated wood samples has changed into hydrophobic since the water contact angles exceed 90° and are equal to 113°, 105°, 100°, 132°, 122°, and 120° for F1, F2, F3, FS1, FS2 and FS3, respectively. Moreover, the wetting angles were higher for the samples initially covered with silica nanoparticles and then with OFTES-based coating. The arrangement of the silica spheres leaves many voids between them which differentiates the wood surface. The combination of the wood surface roughness and the OFTES-based coating of low surface energy causes that most of the air is confined in interstitial voids or in superhydrophobic voids, while the water droplet is first of all in contact with trapped air (Wang et al. 2011). That is why the modified wood surface cannot be wetted with water and has hydrophobic properties. For the samples coated with the layers based on OFTES/TEOS (F2, F3, FS2 and FS3), the wetting angles are lower than those observed on the surfaces coated with the material based only on OFTES (F1 and FS1). Upon the modification of wood surface with OFTES-based coating, the molecules of the above silane are oriented so that the alkoxysilyl groups are attached to the wood surface, while the fluoroalkyl groups are oriented outside. When the material with addition of TEOS is used, some of the fluoroalkyl chains are covered with a silica layer.

To evaluate the durability and the permeability of the applied coatings, water absorption was measured for all wood samples, and the results are summarized in Table 3.

The data presented in Table 3 indicate that the bare wood absorbed much water—its mass increased by over 50% after 24 h. When wood was covered with silica nanospheres according to the procedure developed by Wang et al. 2011 (sample FS0), water sorption decreased only slightly (statistically negligible result considering the standard deviation values) which points to the high porosity and discontinuity of the produced coating and is consistent with the results of SEM and WCA analyses performed for the discussed sample. The impregnation of bare wood samples with a solution containing as little as 5% of OFTES (sample F1) enabled a more pronounced (about 15%) reduction in water absorptivity caused by the increased hydrophobicity of the sample (see Table 2). The combination of both methods of wood surface modification (deposition of silica nanoparticles followed by the impregnation with 5% solution of OFTES) resulted in a further decrease in water sorption by the FS1 sample to less than 20%. Both the reduction in water absorptivity and a significant increase of WCA

Table 3 Comparison of water absorption for bare wood and coated samples

Sample	Water absorptivity (%)				
	Spec. 1	Spec. 2	Spec. 3	Avg.	STD
Bare wood (F0)	53.67	43.04	60.43	**52.38**	**7.16**
FS0	45.78	42.56	48.72	**45.69**	**2.52**
F1	36.92	37.98	36.28	**37.06**	**0.70**
F2	16.23	17.69	14.32	**16.08**	**1.38**
F3	18.68	17.23	18.22	**18.04**	**0.60**
FS1	18.09	17.68	19.68	**18.48**	**0.86**
FS2	21.09	25.28	26.94	**24.44**	**2.46**
FS3	26.32	27.11	25.08	**26.17**	**0.84**

observed for the FS1 sample are the result of synergistic interaction between silica nanoparticles and fluorosilane that leads to the formation of hierarchical raspberry-like structures on the surface of the discussed sample (Yu et al. 2017). Similar or even slightly higher extent of water sorption reduction has been observed for the F2 sample coated with a solution comprising of 5% of OFTES and 22% of TEOS. In this case the observed phenomenon should be attributed to the formation of a thicker, continuous and hermetic layer as a result of hydrolysis and co-condensation of both silanes used. Taking into consideration the results obtained for the samples F2 and FS1, we could expect that the combination of both approaches (the deposition of silica nanoparticles and impregnation with a solution of OFTES and TEOS) would result in a further decrease in water sorption by wood samples. Unfortunately, water absorptivity of the FS2 sample, prepared in the above way, increased by at least 4 to 6% compared to FS1 and F2 samples, respectively. This undesirable effect can be explained by the formation of extensive, disordered multilayer coating which although prevents the penetration of water into the wood interior but, at the same time, is porous enough to retain water. An attempt to extend the time of wood sample impregnation with the solution of both silanes has also proved to be ineffective. Averaged water absorbability values measured for F3 and FS3 samples were insignificantly (considering the standard deviation values) lower than those measured for the samples F2 and FS2.

Conclusions

3-(2,2,3,3,4,4,5,5-octafluoropentyloxy)propyltriethoxysilane alone or in combination with tetraethoxysilane and/or silica nanoparticles was successfully employed in the preparation of hydrophobic protective coatings on the wood surface. Two strategies for the intensification of siloxane coating protective properties have been compared. It has been proved that both approaches enable the formation of durable protective coatings, chemically bonded to the wood surface (Wood-O–Si bonds formation). Taking into consideration the results of water contact angle and absorbability measurements as well as the complexity of the tested procedures, the single-stage impregnation with the solution of 3-(2,2,3,3,4,4,5,5-octafluoropentyloxy)propyltriethoxysilane and tetraethoxysilane should be regarded as more effective.

Compliance with ethical standards

Conflict of interest There is no conflict of interest.

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