

The fatty acids based organofunctional silane protective coatings for concrete

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Received: 25 March 2020
Accepted: 05 August 2020
Available on line: 10 March 2021

ABSTRACT: The possibility of using free fatty acids for the synthesis of new organofunctional silanes is shown. In nature, fatty acids occur in the form of esters with glycerin (fats) and are widely used for production of soap, oil paints, medicines and cosmetics. Of particular interest in this study was the application of organosilicon derivatives of oleic acid for production of coating that would cover the surface of concrete and protect it from water permeation. As a result of proposed silanization, the concrete surface acquired hydrophobic character with the wetting angles up to 115°, and the concrete absorbability was reduced by up to 93%.

KEYWORDS: Fatty acids; Sol-gel processes; Organically modified silanes; Concrete; Protective coatings.

Citation/Citar como: Szubert, K. (2021) The fatty acids based organofunctional silane protective coatings for concrete. Mater. Construcc. 71 [341], e238 <https://doi.org/10.3989/mc.2021.03420>

RESUMEN: *Revestimientos protectores de silano organofuncional a base de ácidos grasos para el hormigón.* Se muestra la posibilidad de usar ácidos grasos libres para la síntesis de nuevos silanos organofuncionales. En la naturaleza, los ácidos grasos se encuentran en forma de ésteres con glicerina (grasas) y son ampliamente usados para la fabricación de jabones, pinturas de aceite, medicamentos y productos cosméticos. En este estudio fue de particular interés la aplicación de derivados organosilíceos del ácido oleico para la producción de un revestimiento que cubriera la superficie del hormigón y lo protegiera de la permeación del agua. Como resultado de la silanización propuesta, la superficie del hormigón adquirió carácter hidrofóbico con los ángulos de mojado hasta 115°, y su capacidad de absorción se redujo hasta en un 93%.

PALABRAS CLAVE: Ácidos grasos; Procesos sol-gel; Silanos modificados orgánicamente; Hormigón; Revestimientos protectores.

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such as fatty acids, their salts (soap), vegetable oils, wax emulsions and animal fats, were commonly used concrete additives in ancient Rome. Ancient treatises (e.g. Vitruvius, Pliny) mention the use of linseed oil as an additive or as a protective treatment for mortars and other building materials to improve hydrophobicity. Malinowski (19) studied the Caesarea Roman aqueduct and states that some type of oil was added as recommended by Vitruvius. A recent study enabled the detection of linseed oil in the mortar beneath the mosaics of the vaults of Saint Peter's Basilica that was also cited in ancient recipes related to the construction of the basilica (20). The fatty acids derivatives as a hydrophobic agents change the surface tension in pores and cracks, which limits water permeation (18, 21, 22). The chemical structure and properties of fatty acids make them suitable for addition to concrete. Long-chain fatty acids derivatives (oils, soaps) can be added to concrete, where they precipitate as insoluble calcium salts. This deposit gives a hydrophobic coating to the capillary surface, and also blocks some pores in fresh concrete. The pore system that develops during the later hydration steps (> 24 hours) is not affected by this sediment, hence the saturated permeability is not reduced. (23). The carboxyl group can be attracted to the positively charged colloid particles in concrete in a way similar to attraction of carboxyl group in polycarboxylate ether (PCE) which is a popular superplasticizer (24). Moreover, liquid fatty acids have sufficiently high surface tension ($2-3 \cdot 10^{-4}$ N/m) to be retained in composite material (25). Some admixtures tend to entrain air, leading to a permanent reduction in strength conversion (23). Due to the reduced movement of moisture in the concrete containing these admixtures, moisture and efflorescence can be eliminated. This group of materials will restrict the flow of water through the dry concrete which would normally occur by capillary action rather than by external water pressure. In general, all these materials are believed to give the concrete surface hydrophobic properties and can block the pores. The detailed mechanism is unclear, but it has been suggested that the hydrophobic effect is related to the electrostatic charge transferred to the capillary walls. Justnes et al. (26) tested a number of vegetable oils as hydrophobic agents in mortars. They were dispersed in water and added to the cement. Vegetable oils hydrolyzed in the presence of hydroxides in pore water. Cheap canola oil seemed to be most effective.

Our earlier papers present the synthesis of alkoxy-silyl derivative based on rapeseed oil by the reaction of nucleophilic substitution of 3-chloropropyltrimethoxysilane with appropriate sodium salts (rapeseed soap) (27). The obtained silane has been used for production of wood (27) and steel (28) surface coat-

ing protecting from the adverse effect of water. The silane obtained according to the latter procedure was dark in color as a consequence of iodine compounds presence; potassium iodide was used as a catalyst of the nucleophilic substitution reaction. The almost black color of the silane is undesirable for its potential applications in formation of protective coatings as the final color of the protected surface would be changed. That is why alternative methods for silane synthesis have been searched for.

In this paper we report on an alternative method of synthesis of the above-mentioned silane from the commercially available oleic acid (OPTES - (oleate-propyl)triethoxysilane) and propose its use for making concrete surface coating protecting from water permeation inside its structure. The silane obtained by hydrosilylation of allyl oleate shows light yellow color, which has no undesirable effect on the color of the protected surface. No intensive color change of the reaction mixture indicates no side reactions - chemical decomposition of the compound). Possible side reaction products were removed while purification, additionally NMR analysis showed no presence of decomposition products.

2. MATERIALS AND METHODS

2.1. Materials

The used reagents were purchased from Sigma-Aldrich and used without further purification. Concrete samples were made of Portland concrete type 32.5 (GÓRAŹDŹE CEMENT S.A., Poland) consistent with EN 197-1 (29), gravel with a maximum grain size of 16 mm and sand with a maximum grain size of 4 mm (Kruszgeo, Poland). Water for concrete preparation was taken from water supply system.

2.2 Synthesis of Oleic acid based silane OPTES

In the experiment we used OPTES silane obtained from the commercially available oleic acid of natural origin (natural, Sigma-Aldrich). Oleic acid belongs to monounsaturated fatty acids, it is present in large amounts in vegetable oils, e.g. olive oil and rapeseed oil (30). The synthesis of OPTES runs in two stages. At first oleic acid is subjected to esterification reaction with allyl alcohol to give allyl oleate, which is then subjected to hydrosilylation with triethoxysilane to give the desired OPTES. The OPTES structure is shown below (Figure 2).

2.2.1. Synthesis of Allyl Oleate

Concentrated sulfuric acid (1 mL) was added on vigorous stirring to a solution of oleic acid (30 g,

0.1 mol) in allyl alcohol (100 mL) and stirred under reflux overnight. After this time, the mixture was evaporated under reduced pressure and diethyl ether (100 mL) was added to the crude product. Then the mixture was washed thrice with brine (3x75 mL). Separation was difficult when the organic layer was washed with water, a stable suspension was formed. Separation was easier with brine added. Additionally, wash with brine allows to remove large amounts of water than may be dissolved in the organic layer. The allyl oleate solution in ether was dried with magnesium sulfate overnight, filtered and diethyl ether was evaporated under reduced pressure (29.7 g, yield: 92%).

2.2.2. Synthesis of the OPTES silane via hydrosilylation reaction

The platinum Karstedt catalyst (9×10^{-7} mol of Pt) was added to the mixture of allyl oleate from the previous step (29.7 g, 0.09 mol) with triethoxysilane (17.85 g, 0.11 mol) followed by heating to 80 °C for over 1 h. After the reaction mixture was cooled down, the excess of triethoxysilane was evaporated under vacuum to give the product as a yellow liquid (43.5 g, yield 99%). Results of NMR analysis of the product confirmed its structure and purity:

^1H NMR (C_6D_6 , 298 K, 500 MHz) δ = 0.64 (t, 2H, SiCH_2 -); 0.87 (t, 3H, $-\text{CH}_3$); 1.22 (t, 9H, Si-O-CH_2 - $\underline{\text{CH}_3}$); 1.26-1.30 (m, 20H, $-\text{CH}_2$ -); 1.61 (m, 2H, Si-CH_2 - $\underline{\text{CH}_2}$ -); 1.73 (m, 2H, C(O)-CH_2 - $\underline{\text{CH}_2}$ -); 2.00 (m, 4H, $-\underline{\text{CH}_2}$ - CH=); 2.28 (t, 2H, $\text{C(O)-}\underline{\text{CH}_2}$ -); 3.81 (q, 6H, $\text{Si-O-}\underline{\text{CH}_2}$ - CH_3); 4.03 (t, 2H, $-\text{CH}_2$ - O-C(O)-); 5.33 (m, 2H, $-\text{CH=CH-}$) ppm.

^{13}C NMR (C_6D_6 , 298 K, 126 MHz) δ = 6.53 (SiCH_2 -); 14.06 ($-\text{CH}_3$); 18.26 (Si-O-CH_2 - $\underline{\text{CH}_3}$); 22.23-34.31 ($-\text{CH}_2$ -); 58.36 ($\text{Si-O-}\underline{\text{CH}_2}$ - CH_3); 66.24 ($-\text{CH}_2$ - O-C(O)-); 129.68, 129.91 ($-\text{CH=CH-}$); 173.77 (C=O) ppm.

^{29}Si NMR (C_6D_6 , 298 K, 99 MHz) δ = -45.89 ppm.

2.3. Concrete preparation procedure

The concrete samples were made of a mixture containing 1295 kg/m³ of coarse aggregate (gravel),

595 kg/m³ of fine aggregate (sand), 380 kg/m³ of cement and 190 kg/m³ of water. The ratio of free water to cement (w/c) was set to 0.5. Fresh concrete was poured out and subjected to vibrations in the form of cube of the size 100x100x100 mm. The cubic samples were demolded after 24 h of curing, then they were placed in a curing room (20±2 °C, relative humidity (RH) ≥ 90%) for 28 days.

2.4. Preparation of hydrophobic coating

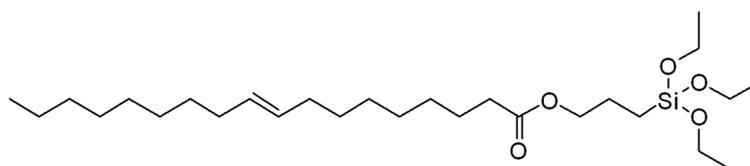
The hardened samples of concrete were washed in water to remove all loose parts and dried for 5 days, then the samples were subjected to silanization. Solutions of OPTES in ethanol were prepared. The first solution (O1) was obtained by adding 25 g of OPTES, 5 g of water and 5 g of concentrated hydrochloric acid to 465 g of ethanol. The second solution (O2) contained 25 g of OPTES, 25 g of tetraethoxysilane (TEOS), 5 g of water, 5 g of concentrated hydrochloric acid and 440 g of ethanol. Next, the solutions were stirred for 3 hours (O1.3 and O2.3) or 72 hours (O1.72 and O2.72). After the indicated time the samples were used for concrete surface silanization. Deposition was carried out in two ways. In the first, concrete were immersed in the solutions for 1 hour. After taking out from the solution, the samples were dried at room temperature for 24 hours. In the second, the solutions were applied using a brush on the surfaces of concrete samples and repeated after 2 hours. Finally, the concrete samples were dried at room temperature for 24 hours also.

The consumption of the silane solution was calculated from the weight loss of the OPTES solution (g) by the silanized surface area (m²).

2.5. Analyses and measurements

The NMR analyses (^1H , ^{13}C and ^{29}Si NMR) were carried out using a Bruker Avance III 500 MHz spectrometer, samples for analysis were prepared in chloroform-d (CDCl_3).

Scanning electron microscopy (SEM) images were taken on a FEI Quanta 250 FEG microscope working in high vacuum mode with 10kV accelerating voltage. EDS Octane SDD detector (EDAX) with electron beam energy of 20keV was used for EDS mapping. The smaller concrete cubes (10x10x10 mm) were cut from the samples described in 2.3 and used to take the SEM images.



OPTES

FIGURE 2. The OPTES structure.

The Drop Shape Analyzer Krüss DSA 100 were used for static water contact angle (WCA) measurements. The analyzer was equipped with a software-controlled (DAS4 2.0): x, y, z-axis table, quadruple dosing unit and a camera with 780 x 580 px resolution. A 5µl volume of water droplet was applied for WCA measurement. The obtained WCA values are arithmetic averages of measurements made for 5 drops per sample. The measurements of WCA were performed 30 s after the deposition of a drop on a studied surface. In an additional experiment on the surface of the concrete sample a drop of water containing a dye was placed in order to observe the hydrophobic character of the surface, the drop containing 0.1% solution of methyl orange had a volume of 20 µl.

The liquid water permeability test was applied for determination of the concrete cubes absorbability of water through capillary suction, according to the norm EN 1062-3 (31). The samples were weighed prior to submerging in water and after 24 h in water. The water level on the tray was at 5-10 mm above the bottom of the concrete sample. The liquid water permeability after 24 h (w) was calculated using Equation [1], where Δm_{24} is mass variation before and after 24h of submerging (kg) in water and A is the surface area of the sample (m^2):

$$w = \frac{\Delta m_{24}}{\sqrt{24 \times A}} \left[kg / (m^2 \times h^{0.5}) \right] \quad [1]$$

The silanization solution penetration depth was determined according to the norm EN-1504-2 (32). In order to determine the depth of the silanization solution penetration into the concrete sample, after silanization the concrete cubes were fractured in two parts. Then the fracture surface was sprayed with water, the border between the bright area (the silanized region not wetted by the water) and the dark area (the region wetted by the water) marks the depth of penetration of the silanization solution into the concrete.

3. RESULTS AND DISCUSSION

As mentioned in the experimental part, prior to silanization of the concrete surface with the solutions the latter were stirred for 3 and 72 hours. The time of stirring was chosen on the basis of earlier experiments on silanization of steel and wood surfaces. The OPTES enter the concrete pores and react with their surface according to sol-gel mechanism, Ca/Si-O-Si bonds are formed. From the chemical point of view OPTES (see Figure 2) is an ester of a higher fatty acid and on the concrete surface may also decompose to form calcium oleate, similar to described the use of butyl stearate as an additive in concrete (23). This compound was used in fresh

concrete and reacts slowly to form a water-insoluble calcium stearate. In the case of silanization the concrete surface, the impact of this process should be infinitesimal.

Two methods of protective coatings application were used in the research: by immersing concrete samples in a silane solution and by painting the concrete surface twice with a brush. The immersion method is often used in academic research, but in practice it cannot be used for silanizing the surfaces of large concrete objects. Additionally, both of the applied methods of coating application are characterized by a similar consumption of OPTES. The average consumption of the OPTES in the immersion method was $20.9 \pm 1.0 \text{ g/m}^2$ ($418 \pm 20 \text{ g/m}^2$ calculated for the OPTES solutions), while in the case of painting the concrete surface twice with a brush, it was $22.9 \pm 1.4 \text{ g/m}^2$ ($458 \pm 28 \text{ g/m}^2$ calculated for the OPTES solutions).

Figure 3 presents exemplary SEM images of the concrete before and after silanization. The concrete surface before silanization was rough but uniform. After silanization (sample O1.3) an additional layer covering the porous concrete surface is seen. Comparison of Figure 3a and 3c shows that silanization did not lead to complete filling of the concrete pores. The photos taken at 200x magnification show open pores, both in the case of the unmodified concrete surface (Figure 3a) and in the case of silanized surfaces (Figure 3c). The attached SEM images confirm that OPTES behaves like a typical hydrophobic impregnation agent (6, 32). Figure 3d taken at a greater magnification (10kx), shows characteristic crackings and fissures, typical of the silica structures obtained by the sol-gel method (27), in the layer covering the concrete surface.

Figure 4 presents exemplary EDS mapping of carbon, silicon and calcium atoms present on the concrete surface. The light regions correspond to the sites with carbon, silicon and calcium atoms, while the dark regions correspond to the areas without these atoms. The images of unmodified concrete reveal the dominant presence of silicon and calcium in the concrete mixture. Additionally, silicon atoms dominate in areas with a deficit of calcium atoms. After silanization, EDS images show much greater content of carbon, which comes from OPTES, it can be seen that the regions with carbon atoms correspond with regions containing silicon atoms. Also the content of silicon is greater in the sample modified with silane in the contrast to unmodified concrete. Comparing the EDS mapping of silicon and calcium atoms on the concrete surface after silanization, can be noticed that these atoms also appear in the same regions (see mapping of silicon and calcium on the surface of unmodified concrete), which indicates that the calcium-rich areas are also covered with the siloxane layer.

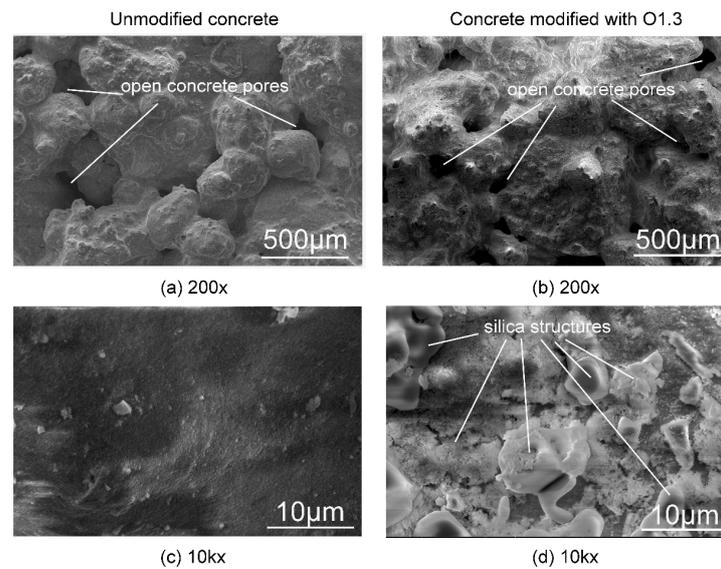


FIGURE 3. SEM image of the unmodified concrete (a, c) and concrete with the modified surface, sample O1.3 (b, d).

Usually to increase the concrete hydrophobic character the use of concentrated silane solutions and higher silan consumption is needed (5, 16, 17), for OPTES it was sufficient to use 5% alcohol silane solutions. The WCA measurements are collected in Table 1.

TABLE 1. Water contact angle (WCA) values of concrete without and with OPTES treatment.

Sample	WCA/degree
concrete	-
Immersion	
O1.3	114.6±4.52
O1.72	113.5±5.94
O2.3	112.1±5.07
O2.72	112.1±5.27
Brush painting	
O1.3	104.8±5.77
O1.72	113.6±1.53
O2.3	101.4±7.41
O2.72	103.6±4.24

Correct measurement of the contact angle on the surface of unmodified concrete was impossible because the water droplet was immediately spilled and absorbed into the sample, which confirmed high water absorbability and strongly hydrophilic character of concrete. The contact angles measured for the concrete surface modified with alcohol solutions

of OPTES were above 101° , which confirms the hydrophobic character of the modified surfaces. Moreover, it should be emphasized that the contact angles were measured at 30 seconds after placing water droplet on the surface and during this time the water droplet did not change shape (did not spill out) and its volume did not decrease (water was not absorbed). For all modified concrete samples the average contact angles were similar. The slightly lower values of the angles were obtained for the concrete surface modified by brush painting, however, these values are still within the standard deviations. Figure 5 presents the water droplets dyed with methyl orange deposited on the unmodified and silanized concrete surface, immediately after droplet deposition and after its evaporation. As mentioned earlier, the water droplet deposited on the unmodified concrete surface immediately spills over a relatively large irregular area and disappears (gets absorbed), Figure 5a. While a drop of water placed on the surface of the concrete after silanization maintains its regular shape with a small contact area between the drop and the concrete surface (Figure 5b). After complete evaporation of the water, on the surface of unmodified concrete (Figure 5c), an irregularly shaped dye remained, the surface of the concrete coated with the dye is smaller than the area immediately after the drop of water with methyl orange, which indicates a strong water capillary rise. Whereas, a regular circular stain of dye remained on the concrete surface after the droplet was evaporated (Figure 5d). The behavior of water drops on the surface of unmodified and silanized concrete were as expected and consistent with the previous results of contact angles measurements. It should be emphasized that all modified concrete samples behaved in a similar way.

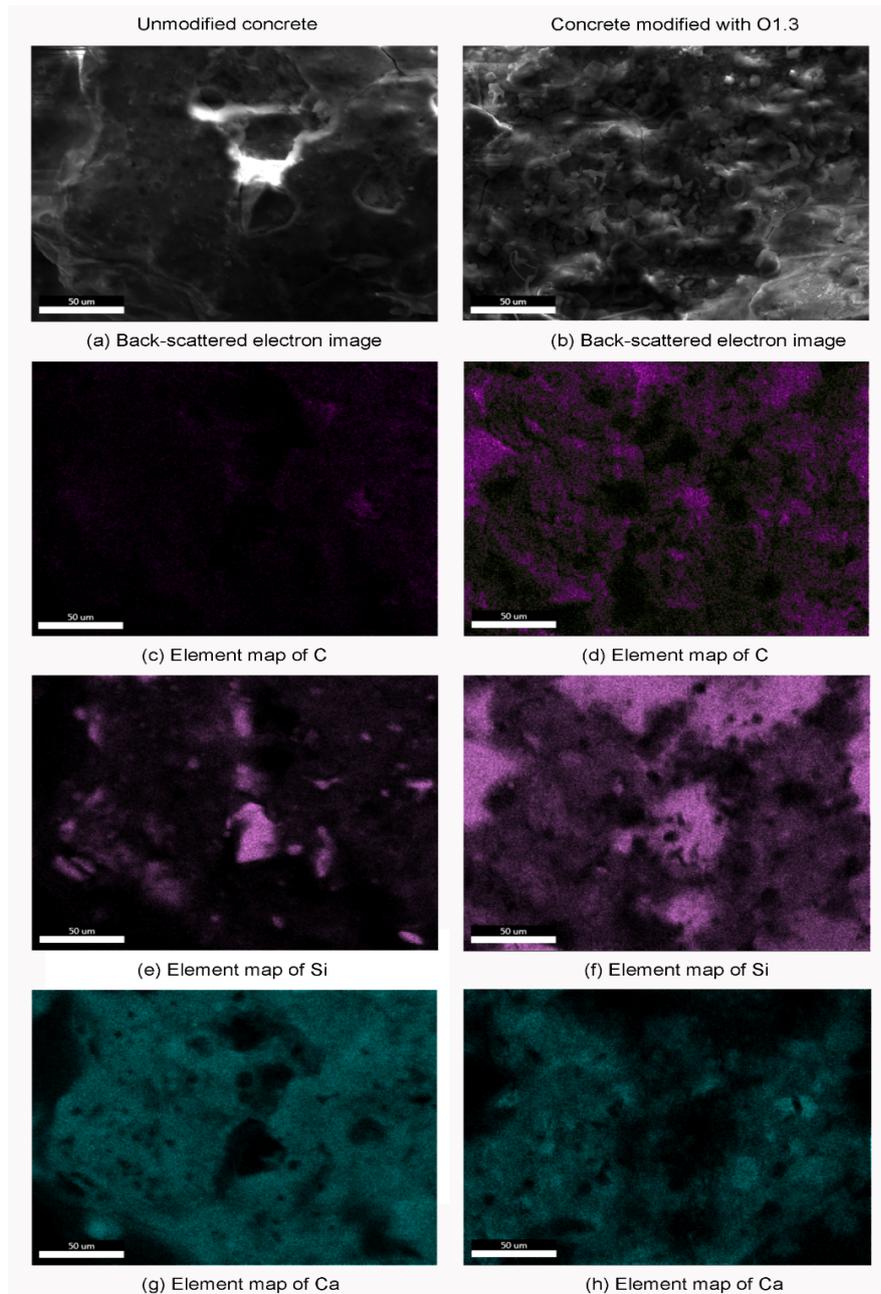


FIGURE 4. EDS mapping of the elements occurring on the surface of unmodified concrete (a, c, e, g) and silanized sample O1.3 (b, d, f, h).

As mentioned above, the absorbability measurements were performed according to EN-1062-3 (31). The water absorbability (w) data are summarized in Table 2.

The result obtained for the unmodified concrete was similar to that obtained by Baltazar et. al. (33), while the water absorbability coefficients obtained for the samples subjected to silanization are indicative of a significant restriction of water transport into the inner structure of concrete. For samples O1.3 and O1.72 subjected to impregnation by immersion with solutions containing OPTES, the wa-

ter absorbability was reduced by 92.7% and 89.5%, respectively. Longer time of stirring of the solution with OPTES slightly reduced the barrier effect of the coating produced. For samples O2.3 and O2.72 coated with the material containing an addition of TEOS, the water absorbability was reduced by about 93%, the effect of extended time of stirring was also insignificant and could be neglected. According to the results the coatings obtained from the solutions containing an addition of TEOS show a little better barrier properties. For these coatings a longer time of stirring of the relevant solutions had less effect on

the results obtained. In the case of coatings obtained as a result of brush painting, similar water absorbability were obtained. An improvement in barrier properties can be noticed in the case of samples mixed for 3 hours, for both tested solutions, a reduction in water absorbability by 95% was achieved. When the solutions mixed for 72 hours were used, the results were slightly worse compared to those obtained by immersion. Analyzing the obtained results, it can also be noticed that the addition of TEOS has a beneficial effect on the barrier properties of coatings obtained from solutions with longer mixing time.

TABLE 2. Water permeability (w) after 24h of immersion of concrete samples without and with OPTES treatment.

Sample	w [kg/m ² h ^{0.5}]	Relative improvement in absorbability [%]
concrete	0.4777±0.0420	-
Immersion (20.9±1.0 g/m²)		
O1.3	0.0347±0.0012	92.7
O1.72	0.0503±0.0046	89.5
O2.3	0.0323±0.0025	93.3
O2.72	0.0363±0.0012	92.5
Brush painting (22.9±1.4 g/m²)		
O1.3	0.0253±0.0021	94.8
O1.72	0.0617±0.0040	87.0
O2.3	0.0240±0.0017	95.0
O2.72	0.0423±0.0020	91.2

The depth of silanes penetration into concrete was measured according to EN-1504-2 (32). The cubes of concrete were cut and the surfaces of the break were sprayed with water. Figure 6 shows examples of the wet cutting surface, the surface coated with silane was not wetted and was much brighter than the deeper layers of the concrete sample which were well wetted with water. In all samples of modified by immersion concrete, the silanizing solutions penetrated to the depth of 4-5 mm, while in the case of surfaces painted with a brush, silane penetrated to a lower depth (3-4 mm).

4. CONCLUSIONS

The silane obtained as a result of hydrosilylation of allyl oleate shows only slight coloring which has no effect on the color of the material coated, in contrast to almost black silane obtained according to the earlier proposed method of its synthesis. It is especially important considering the potential application of this type of hydrophobic impregnation for the protection of decorative building materials, such as architectural concrete, bricks or stones. The use of OPTES silane reduced the water absorbability of modified concrete by up to 95%. It should be emphasized that a good barrier effect was achieved at low silane concentrations, several times lower than previously described in the literature. It has been shown that extended time of stirring the solutions containing TEOS prior to their application for silanization of concrete surface has insignificant effect on the parameters of the coatings obtained. It seems that the addition of TEOS stabilizes the solutions

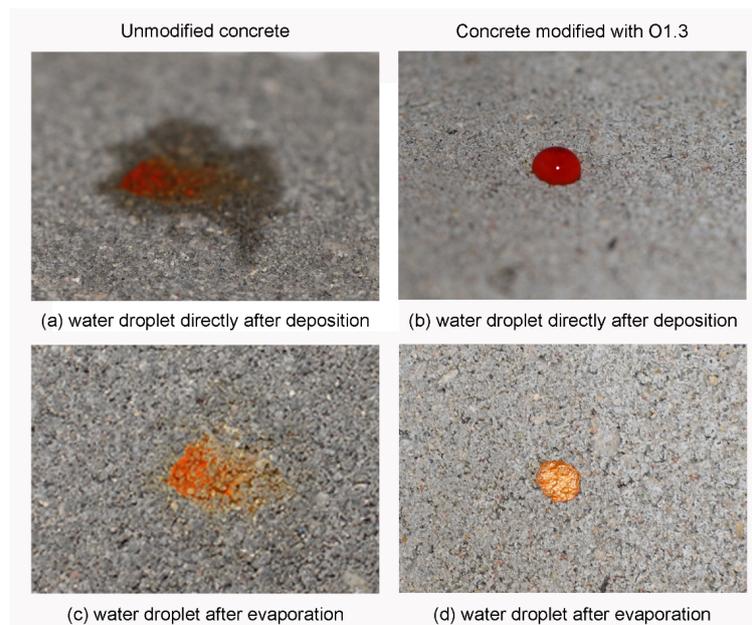


FIGURE 5. Images of a water droplet dyed with methyl orange placed on the surface of unmodified (a, c) and modified by O1.3 concrete (b, d); directly after deposition and after evaporation.

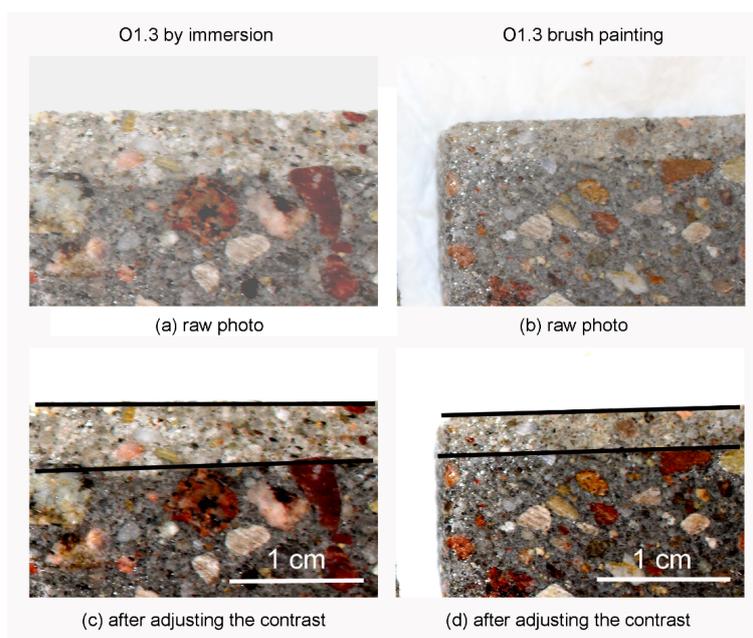


FIGURE 6. Results of penetration depth revealing by water spraying on the cut concrete specimens.

and permits their use for a longer time. Further research is required to determine the durability of alcoholic OPTES solutions and coatings based on them. The results presented open new possibilities of using products of natural origin for the synthesis of organosilicon derivatives and their use for production of protective coatings stronger interacting with the surface of the material coated. Of course, the precise determination of the practical applicability of OPTES requires further research, especially aging tests.

ACKNOWLEDGMENTS

Author thanks Nuria Miguel from University of Zaragoza (in 2019/2020 as Erasmus Student working on her Bachelor Thesis at AMU) for Spanish translation. Author would like to express his gratitude to Center for Advanced Technologies in Poznan for giving us the opportunity to perform Scanning Electron Microscope images and Energy Dispersive Spectroscopy spectra. This work was supported by funds from the National Science Centre (Poland) granted on the basis of decision number DEC-2013/09/D/ST5/03845.

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