

Modification of Concrete Surface with Higher Fatty Acids

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ABSTRACT

The paper's research focuses on the development of novel hydrophobizing agents and the demonstration of their efficiency on a concrete surface. The starting materials are based on natural oils, water-soluble silanes and siloxanes, and/or tap water. Aqueous preparations have qualities that limit the influence of volatile organic compounds (VOCs) on the environment since they solely include biodegradable components. According to research, the higher fatty acids obtained from vegetable oils and derived from the glycerin phase can be employed as a component of concrete hydrophobizing agents while matching the standard requirements for such agents. Analysis of the usage of vegetable oil as a basis ingredient in the manufacturing of industrial substances shows that it is biodegradable with at least 95% certainty. The reference concrete after the frost resistance test showed a weight loss of 1.8%. In the case of hydrophobization, the weight loss was 33.3 to 72% less than the reference samples. In the case of concrete hydrophobized with the glycerin agents, the salt crystallization occurred inside the structure of the material without causing any damage, with the reference concrete showing a weight loss of 0.8%.

Keywords: contact angle; higher fatty acids; hydrophobic agent; hydrophobization; water tightness; vapor permeability.

INTRODUCTION

In the erection process of new concrete buildings and engineering structures from concrete and reinforced concrete, the most important thing is that they serve for the entire period for which they were designed. Standard-compliant designs are important, but also safeguards against external influences must be applied at the design stage. Maintaining structures in good condition contributes to reducing CO₂ emissions, as there will be no need to build new constructions. Cement, as the main component of concrete in the construction industry, is responsible for 8% of anthropogenic emissions [1], especially CO₂ emissions [2]. Also, the materials used to protect the structure

from external conditions should be in line with the vision of sustainable construction [3]. It is important to implement and use green innovations.

Concrete is recognized as one of the most durable construction materials [4]. It also provides very good protection for the reinforcement that is placed in it [5]. Unfortunately, despite its excellent properties, it can unfortunately deteriorate. Three main factors affect this, including the cover, the embedded concrete quality, and cracks. This allows external harmful substances to penetrate the concrete, including chloride ions [6], air, and water. The important thing is to keep in mind that the deterioration of concrete is not the result of the influence of a single process or factor. Some factors such as freezing–thawing cycles

or carbonization do not individually degrade the structure but can also contribute to a synergistic effect [7]. Concrete suffers not only from physical stress, such as freeze-thaw cycles or wetting-drying cycles, but also from chemical attack caused by aggressive substances contained in water or air [8]. Through this, it can be deduced that the external environment is basically one large center of harmful factors that can cause damage to concrete structures.

In general, for the protection of existing concrete structures, a distinction can be made between passive methods – “preventive solutions” and active methods – “therapeutic solutions”. In the case of passive methods, measures are used to maintain the current state and prevent further deterioration of the concrete, such as the use of coatings. In the case of “therapeutic solutions”, the key is to mitigate or stop the destructive processes (difficult to do in practice) [9]. Surface protection of concrete structures [10,11] has a unique superiority over other available methods [12,13]. The reason for this is because surface-applied coatings can be used on existing structures, on objects that are already in use, and can also be used as a system to protect and repair already damaged ones. In addition, they can perform decorative functions and prevent degradation of concrete under the influence of ultraviolet radiation. The general mechanism of coating the concrete surface is to reduce the penetration of aggressive agents such as water, oxygen, carbon dioxide or chloride ions [14]. Among other things, the following are used to protect the surface of concrete: one- and two-component protective coatings, mortars for surface priming, wax and acrylic care products, protective paints for concrete, and hydrophobizing agents. Before selecting the appropriate protection, it is essential to consider the composition of the agent employed, as some of them include hazardous VOCs [15]. The term VOC refers to a wide range of carbon-containing chemicals. At room temperature, VOCs are typically liquids or solids, with high vapor pressure, meaning that they readily evaporate to gaseous form. In recent years, VOCs have received increasing attention as pollutants and health hazards [16]. Therefore, products should be used that contain biodegradable and environmentally harmless ingredients, but also provide very good protection against external factors. In addition they should be easy to apply and have a long service life.

It is tough to select the appropriate surface protection due to the huge variety of products on the market. It is critical to guarantee that the product does not obstruct vapor permeability while also not allowing dangerous compounds to enter the structure. Hydrophobization is a very good way of the concrete surface protection, which has been confirmed in many publications [17–21].

Also, the use of an organic coating can create a highly chemically resistant to the penetration of aggressive agents, a continuous layer on the concrete surface. Silanes, siloxides and similar chemicals can create a water-repellent layer due to their ability to penetrate the pores of concrete and react with the water contained within [22].

Using higher fatty acids in the hydrophobizing agents production process is a novelty in the study conducted by the authors. Edible oils have been used to develop non-toxic and biologically degradable formulations. Higher carboxylic acids are compounds that contain a long carbon chain (several carbon atoms) and a group characteristic of carboxylic acids –COOH. Higher carboxylic acids are also called as the fatty acids. Fat molecules contain fatty acid residues in their composition. In order to obtain fatty acids, vegetable oils, such as coconut oil, sunflower oil, or canola oil, can be modified [23]. Because of their hydrophobic characteristics, they may be utilized to make mold release agents [24], making them ideal for use in hydrophobizing formulations. The authors in their previous publications [25,26] have shown that the application of higher fatty acids on the concrete surface does not cause discoloration of its surface, or deterioration of the properties of the finished material. Furthermore, while the publication [23] discusses the possibility of utilizing vegetable oil in the construction business, there are no reports in the literature on the usage of higher fatty acids for the concrete surface protection.

MATERIALS AND METHODS

Materials

Concrete

The test material was ordinary concrete of the C25/30 class. For its preparation the following raw materials were used: CEM I 42.5 R (Chełm cement plant, CEMEX Polska Sp. z o.o., Poland) as a binder, gravel aggregate as a coarse

aggregate, obtained from the Dziergowice Mineral Raw Materials Mine, having particle size distribution between 2–16 mm, quartz sand (ordinary sand) – 0–2 mm graining – from the Gęsia Wólka Mineral Raw Materials Mine as fine aggregate, and tap water. Table 1 shows the chemical composition of the cement used, and Table 2 shows the concrete recipe.

In addition to its stable physico-chemical properties, the cement is characterized by a high resistance to aggressive chemical substances, a fast setting time, a final and early strength at high level, and a low alkali content. Therefore, a ready-mixed concrete is often produced with it. Table 3 summarizes the detailed physico-chemical parameters of cement.

A mechanical mixer was used to slowly mix the dry ingredients for 2 minutes. Water enriched with a superplasticizer was gradually applied to the concrete mixture, in order to prevent segregation of mixture components. Mixing was continued for 5 min. The concrete mixture was compacted by means of a vibrating table (at the 50 Hz frequency of vibration) to prevent a cement lactance and to prevent the ingredients segregation. After 24 hours the samples were demolded. Then they were conditioned for 28 days in water at $20 \pm 5^\circ\text{C}$.

Hydrophobizing agents

New hydrophobizing agents based on natural oils, water-soluble silanes and siloxanes and/or tap water were used in the research. The individual configurations of the hydrophobizing preparations used are presented in Table 4. The characteristics of the silicon-organic compounds used in hydrophobizing agents are presented in Table 5.

The material for the study was vegetable oil of industrial origin purchased in Poland. The oil used in the production process was characterized by the following parameters: FFA – 4%; AN – 5 mgKOH/g and H_2O up to about 3%. The obtained products were given the names Bioecobase and Bioecobase-g. The Bioecobase and Bioecobase-g manufacturing methods are evaluated at the moment within the patent application (P.437754 of 30/04/2021). Therefore, the authors in this paper will give an overview of the production process

and the requirements that are placed on the raw materials used in their manufacture.

When preparing the Bioecobase and Bioecobase-g, the method includes the steps:

- inedible vegetable oils, which were formed, for example, due to an improper storage, are heated; the input product for the production of vegetable oils is, for example, soybeans, sunflowers;
- a potassium and methanol catalytic mixture is prepared;
- triggering a reaction, simply by mixing the oil prepared in the first step with a catalytic mixture, which results in a post-reaction mixture.

The resulting reaction mixture was directed to a phase separator, where, due to the sedimentation, it is separated into two layers, the upper of which is subjected to a bleaching process in a filter filled with bleaching earth and activated carbon to obtain a finished product with the proprietary name – Bioecobase (WKM-Energia Sp. z o.o., Poland). In a further process to create an agent with hydrophobizing properties, the Bioecobase was mixed (with a slow-speed mixer to prevent the temperature of the mixture from rising), with a polysilicone compound – a methyl-silicone resin based on organic solvents and aliphatic hydrocarbons.

Methods

Preparation of specimens

To perform the tests, concrete samples of the C25/30 class with dimensions of $10 \times 10 \times 10$ cm were prepared. Table 6 summarizes the main characteristics of the concrete used in the tests.

Dust and other small impurities that may affect hydrophobization quality were carefully removed from the samples.

After being dried to a constant weight, all samples were conditioned at $20 \pm 2^\circ\text{C}$ and RH (relative humidity) equal to $60 \pm 5\%$ for the period of 10 days, before being hydrophobized. After conditioning, samples were maintained at 2% relative humidity, which is recommended by most manufacturers of hydrophobic preparations [4].

Table 1. Chemical composition of cement (% mass)

Component	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Fe_2O	ZnO
CEM I 42.5 R	0.4	1.4	6.6	19.4	0.3	5.2	1.2	61.2	0.4	3.3	0.1

Table 2. The recipe of the concrete tested

Parameter	Unit	Quantity
Cement CEM I 42.5 R	kg/m ³	330
Gravel aggregate (2–8 mm)	kg/m ³	577
Gravel aggregate (8–16 mm)	kg/m ³	655
Quartz sand	kg/m ³	653
Water	kg/m ³	150
w/c = 0.45	–	–

Hydrophobization

After a 10–day conditioning period, the surfaces of concrete samples were hydrophobized. The preparation was used twice to make the samples hydrophobized. The agents were applied twice by brush, one layer after another, so as not to interrupt the capillary action (“wet on wet” method), and then all samples were conditioned for 7–day period in laboratory conditions. This

allow the polysiloxane gel hydrolytic polycondensation process to occur, in the surface structure of the material. Six samples were used for each test to determine the physical properties of the materials.

Research methods

Tests with respect to oxygen biodegradability in aqueous media were performed with the use of the manometric respirometry. Incubation period was equal to 28 days, with access to oxygen, at 22 ± 1°C, with continuous stirring, inside tightly sealed respirometry containers. The concentration of the analyzed material was 100 mg/L, i.e., the sample contained at least 50–100 mg of ThOD/L with the adequate amount of inoculum – up to 30 mg d.m./L and mineral medium. The active sediment for the analyses was collected from an aeration tank at the “Czajka” Water Treatment

Table 3. Physico–chemical properties of the CEM I 42.5 R (according to the manufacturer)

Feature	Unit	Average value
Blaine’s specific surface area	cm ² /g	4124
Volume change	mm	0.9
The beginning of setting time	min	185
The end of setting time	min	240
Compressive strength: after 2 days	MPa	30.5
Compressive strength: after 28 days	MPa	59.4
The insoluble residue	%	0.64
Loss on ignition	%	3.22
Amount of SO ₃	%	2.97
Amount of Cl	%	0.09
Amount of clinker	%	95–100

Table 4. Composition of individual variants of the hydrophobizing agents (A1–A12)

Variant	Quantity [%]						
	Silane 1	Silane 2	Nanosilane	Bioecobase-g	Bioecobase	Methyl silicone resin	Water
A1	33.3	–	–	–	–	–	66.6
A2	33.3	–	–	33.3	–	–	33.3
A3	–	–	50.0	50.0	–	–	–
A4	–	10.0	–	–	90.0	–	–
A5	–	–	–	–	70.0	30.0	–
A6	–	–	33.3	33.3	–	–	33.3
A7	–	30.0	–	–	70.0	–	–
A8	–	–	50.0	30.0	–	–	20.0
A9	–	–	–	–	60.0	40.0	–
A10	–	–	50.0	–	–	–	50.0
A11	–	–	100.0	–	–	–	–
A12	–	–	–	–	–	100.0	–

Table 5. Characteristics of the organosilicon compounds (based on the manufacturer’s data)

	Description	Viscosity Pa·s	Density g/cm ³
Silane 1	Organo-functional, siloxane-based emulsion with almost zero volatile organic compounds (VOC) (Protectosil® WS 610, agent from Evonic, Essen, Germany)	0.012	1.017
Silane 2	Silicic acid ester, insoluble in water SH100 – Protectosil® SH100, Evonik Resource Efficiency GmbH	0.005	1.06
Nanosilane	Organo-functional silane system and water (SC30 – Protectosil, agent from Evonic, Essen, Germany)	0.01	1.02
Methyl silicone resin	Solution of silicone compounds in a solvent (Sarsil – Zakłady Chemiczne “Silikony Polskie” Sp. z o.o. Nowa Sarzyna)	0.028	0.81

Table 6. Properties of the fresh and hardened concrete

Properties	Unit	Average value	SD	CV
Air content in fresh mixture	%	1.75	0.5	0.01
Density of mixture concrete	g/cm ³	2.36	0.2	0.02
Volumetric density ρ_v	g/cm ³	2.23	0.2	0.02
Open porosity P_o	%	10.8	0.7	0.05
Total porosity P	%	12.8	0.21	0.01
Compressive strength	MPa	38.0	0.74	0.11
Tensile strength in bending	MPa	6.1	0.67	0.09

Note: SD – standard deviation, CV – coefficient of variation (%).

Plant in Warsaw. The degree of biodegradability was determined by measuring oxygen consumption and expressed directly as the mg/L BOD. The amount of oxygen absorbed by the sediment microorganisms during the biodegradation of the analyzed material was expressed as a ThOD or COD percentage. The tests showed to be consistent with appendices 1 and 3 to SPO/BS/01/b (rev. 5) and the PN ISO 9408:2005 standard [27].

- BOD – biochemical oxygen demand;
- COD – chemical oxygen demand;
- ThOD – theoretical oxygen demand.

Determination of the wettability of the surface coated with the hydrophobizing agent was performed by the contact angle measurement using a drop of liquid. The tests were carried out on a test rig consisting of an optical goniometer (Data Physics Instruments GmbH, Filderstadt, Germany). To capture images of drops, which were applied to the samples surface, a camera was used. A distilled water was used to measure the contact angle (CA). It was necessary to use a liquid for which the total surface free energy (γ_w) is known. It was used to measure the contact angles θ_w that are appropriate to the surface coatings. A constant volumes of liquid equal to 2 mm³ were used at a surface of samples. It was

done by a micropipette. Taking into account the material heterogeneity, to each sample five drops were used. During the application of each drop, measurements were performed at a temperature of 23.0 ± 1.0 °C [28].

The samples structure as well as the hydrophobic coatings were examined by the SEM – scanning electron microscope (Quanta FEG 250 microscope by FEI, Hillsboro, OR, USA). Also the energy dispersive X-ray spectroscopy (EDS) (EDAX, Mahwah, NY, USA) was applied to measure the local chemical composition during the SEM observations.

In addition, concrete samples with a hydrophobic coating were subjected to other tests presented in Table 7. The table highlights the relevant standards according to which each study was carried out.

The rheological characteristics of the hydrophobizing agents were determined by measurements of their density and viscosity. The PN-EN ISO 2811-1:2016 [26] and PN-EN ISO 2431:2012 [27] was applied in this regard. The Stokes method using an Ostwald viscometer was used to measure the viscosity index η . The room temperature equal to 22.5 °C was at the time of taking the measurements. The average value was obtained from five individual measurements.

Table 7. Properties of the fresh and hardened concrete

Test	Standard
Water absorption	PN-B-06250:1988 [29]
Vapor permeability	PN-EN ISO 7783:2018-11 [30]
Water absorption coefficient caused by the rising capillary action	PN-EN 772-11:2011 [31]
Water tightness	PN-B-06250:1988 [29]
Frost resistance	PN-B-06265:2018 [32]
Resistance to salts crystallization pressure	PN-EN 12370:2001 [33]

RESULTS

The basic rheological characteristics of the hydrophobizing agents

No segregation of ingredients was observed, even after a few days from the moment of producing a new preparation. Preparations containing natural oils changed the color of the hydrophobic agents to a darker, yellow, similar to natural oils. The color of the water-soluble preparations (A1, A2, A6, A8, A10, A11) remained unchanged. Formulations 1 and 2 are white, as that was the color of the Silane 1. Table 8 presents the results of the volume density as well as the viscosity coefficient η of the hydrophobizing agents used.

The newly developed products based on the Bioecobase are characterized by densities lower than 1.0 g/cm³. The water-soluble formulations showed densities greater than 1.0 g/cm³. The lowest dynamic viscosity was obtained by the A11 agent, while the agents A5 and A9 with the Bioecobase and methyl silicone resin had the highest dynamic viscosity (0.045 Pa·s).

Biodegradability test

Figure 1 shows the biodegradability results of a vegetable oil-based liquid with the adopted name the Bioecobase. Based on them, the tested material was found to be aerobically biodegradable in an aqueous environment. In the conducted 28-day experiment, attention was focused on testing the final aerobic biodegradation of the liquid by manometric respirometry according to the OECD 301F guidelines [36]. The recorded test temperature was within the expected range of 22 ± 1 °C. In the toxicity test, biodegradability is equal to 71.9% on day

14, i.e., there was a higher biodegradation level (71.9%) than 25% (calculated based on COD), so it can be concluded that the test material does not have an inhibitory effect on activated sludge. The BOD/COD ratio which correspond to the aerobic biodegradability of the material, on the 28th day of the study, was equal to 95.1%.

Contact angle (CA)

The distilled water was used to measure the contact angle (CA). During the application of drops the room temperature was equal to 22.5 °C. Selected measurements are shown in Figure 2, while the Figure 3 shows the results for all concretes.

The reference concrete surface was completely saturated, CA was less than 2°, which means very good hydrophilicity. For hydrophobization to be considered effective, the CA should be greater than 90°, then the surface has hydrophobic properties. After the application of hydrophobizing formulations, all CAs were greater than 90°. However, formulations based on the nanosilane (A6, A8, A10, A11) and on the methyl silicone resin (A12) made the concrete surface to be superhydrophobic (CA > 120°). This is confirmed by Kang, H. et. al, who showed that CA after hydrophobization of cement mortar surfaces ranged from 126° to 132° [37].

To perform more detailed analysis of the hydrophobizing agents effectiveness, a water absorption test was performed.

Water absorption

Figure 4 presents the water absorption results after 7 days of the study.

Table 8. Density and viscosity results of the mold release agents

Parameter	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12
Dynamic viscosity, Pa·s	0.043	0.043	0.039	0.04	0.045	0.043	0.043	0.044	0.045	0.017	0.01	0.028
Density, g/cm ³	1.02	1.07	1.06	0.95	0.86	1.08	0.93	1.04	0.84	1.01	1.02	0.81

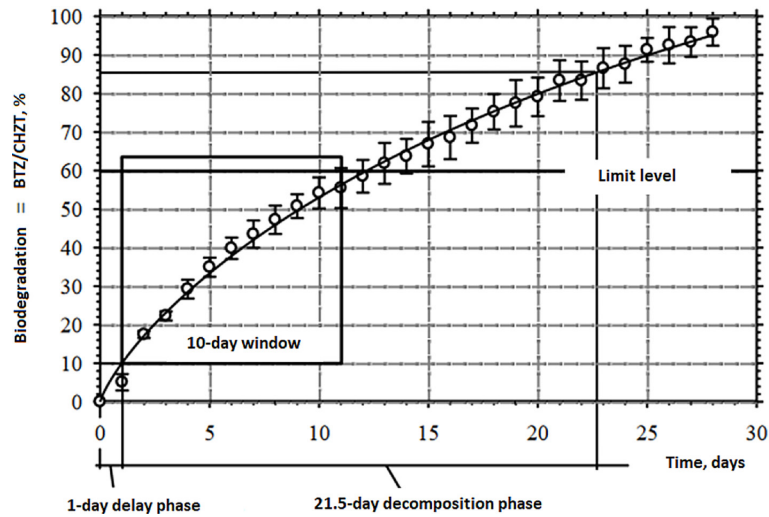


Figure 1. The biodegradation curves of the material tested and reference material, for which the vegetable oil was a base

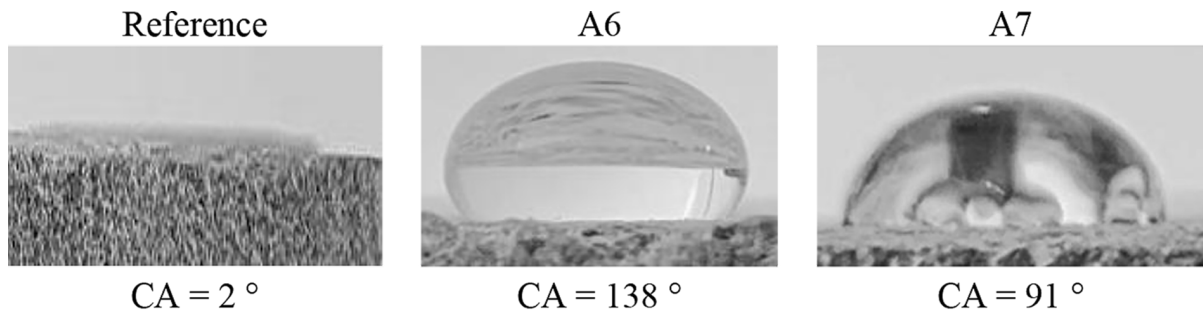


Figure 2. Selected photos of the contact angle measurement

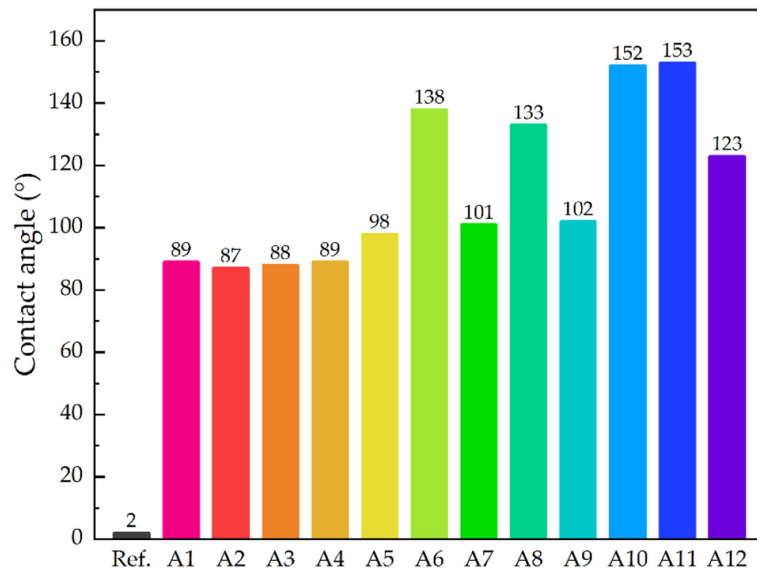


Figure 3. Measurements of the contact angle at the concrete surface

It was observed that very good concrete hydrophobization efficiency was obtained using hydrophobizing formulations numbered A5-A12. Accordingly, formulations with a CA greater than 90° and a water absorption of less than 2%

(formulations A5 – A10) were qualified for further testing. The decrease in concrete water absorption after using these formulations ranged from 52.5% to 75%. In addition, comparative tests were performed with commercial preparations A11 and A12.

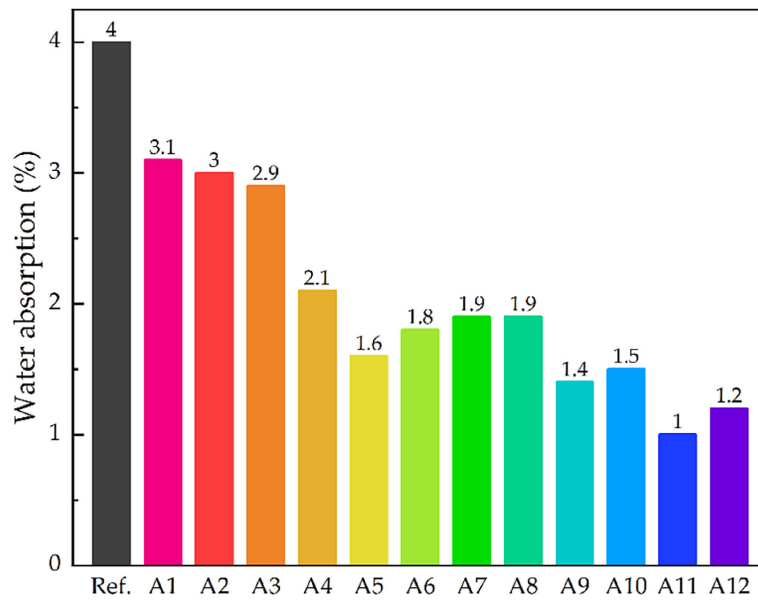


Figure 4. Concrete water absorption

Also other authors [20,21,38–41] confirm the favorable effect of the silanes-based hydrophobization of a surface. As a result of the application of silanes by Szubert et al. [34], the concrete surface achieved very good hydrophobicity with a contact angle of up to 126°, and the concrete water absorption decreased by 96%. The siloxane changes the hydrophilicity of the capillary surface and makes it hydrophobic because it contains hydrocarbons in its structure as demonstrated, among others, by Kang et al. [37], Barnat-Hunek et al. [20,21,25], Maravelaki-Kalaitzaki [43].

Vapor permeability

The “wet pot” method under isothermal conditions was applied to measure the concrete water vapor permeability. The method involves placing

the test samples between two different environments with different air humidity (desiccator) (Fig. 5). The hydrophobic coating was directed toward atmospheric air. One environment was a desiccator with a relative humidity of 50% ± 5%, and the other was the interior of a cup containing potassium nitrate KNO₃, which guaranteed a humidity of about 95% in the cup. The container (cup) was covered with the test sample and sealed circumferentially with epoxy resin. Through regular weighing, moisture losses up to a state of equilibrium, were recorded. The test time was about 10 days, depending on the diffusion through the surface of the material. The coefficient of the water vapor diffusion resistance μ was determined from the formula: $\mu = \delta a / \delta$. The air water vapor transmission coefficient $\delta a = 1.950 \cdot 10^{-10}$ kg/(m·s·Pa). The μ coefficient is given in Figure 6.

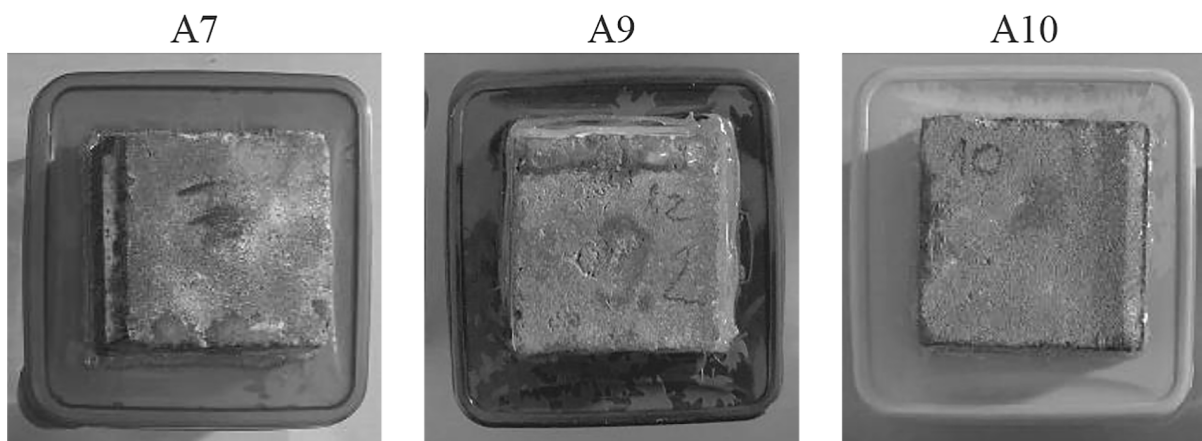


Figure 5. Measurement of the water vapor permeability

The test of the vapor permeability showed that water repellents increased the μ coefficient, with the vegetable oil-based formulation (Bioecobase) and methylsilicone resin in organic solvent (A9) caused the greatest sealing, followed by the water agent A6 (33.3% nanosilane; 33.3% water; 33.3% Bioecobase-g). These are the formulations that resulted in the best water protection. Silane and higher fatty acids form a sealed layer on the sample surface, hindering the absorption of an external water. In addition the water vapor diffusion to the external zone of the sample is limited, which can cause the damage occurrence inside the sample, as reported by Liu and Hansen [39].

The water absorption coefficient caused by the rising capillary action

Figures 7 and 8 presents the results of the test. The application of the hydrophobic agents significantly reduced the absorption coefficient of concrete. The greatest effectiveness was obtained with the A9 formulation (60% Bioecobase and 40% methylsilicone resin), which caused an almost fivefold reduction in the capillary rise of concrete. The commercial A12 formulation achieved similar results. In contrast, the A6 formulation (33.3% nanosilane; 33.3% water; 33.3% Bioecobase-g) reduced the water rise in concrete by more than two times. The reference

A11 formulation achieved the best result in concrete (0.11 kg/m^2) for the water-soluble formulation group. It is more beneficial to implement the surface hydrophobic agents than water-repellent agents (directly applied to the concrete mixture), as stated by Zhu et al. [44].

Water tightness

In water tightness tests, the samples were pressurized up to 0.8 MPa, which is equivalent to the W8 water tightness class taking into account the PN-B-06250 [29]. The water tightness class was tested to be W8, as no water leakage was observed through the samples under the maximum pressure set. After the test, the depth of water penetration was determined on the split samples. The water depth penetration in no sample exceeded 1.5 cm, which should be considered as a very good and satisfactory result (Figure 8).

The effect of hydrophobization on the water tightness results was clearly observed, although hydrophobization generally does not protect concrete from water under pressure. The Bioecobase-based formulations showed greater blockage to water. The best result was obtained for the A9 agent (0.6 cm) and the commercial A12 formulation. Among water-permeable formulations, the best results were obtained for the A6 with Bioecobase-g and nanosilane.

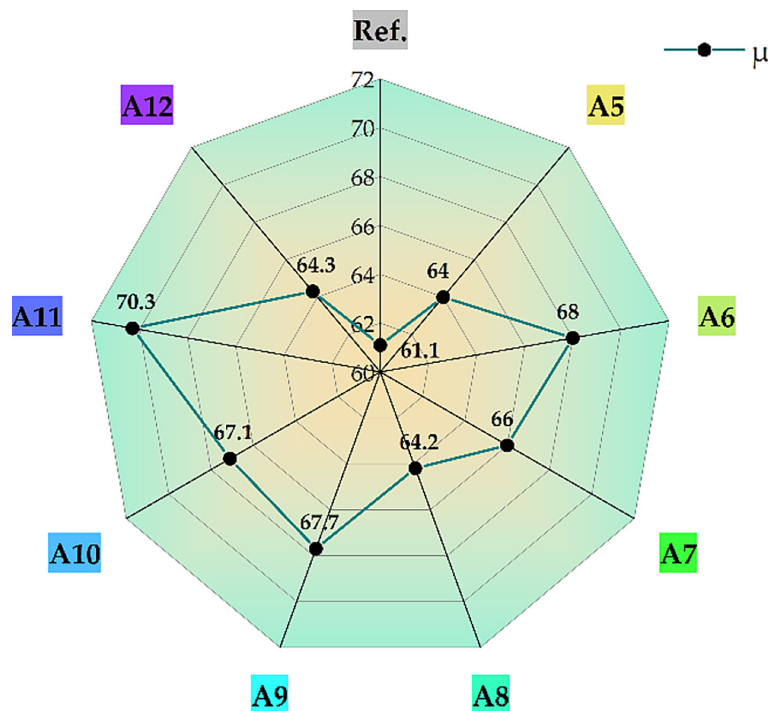


Figure 6. The coefficient of the water vapor diffusion resistance μ (-)

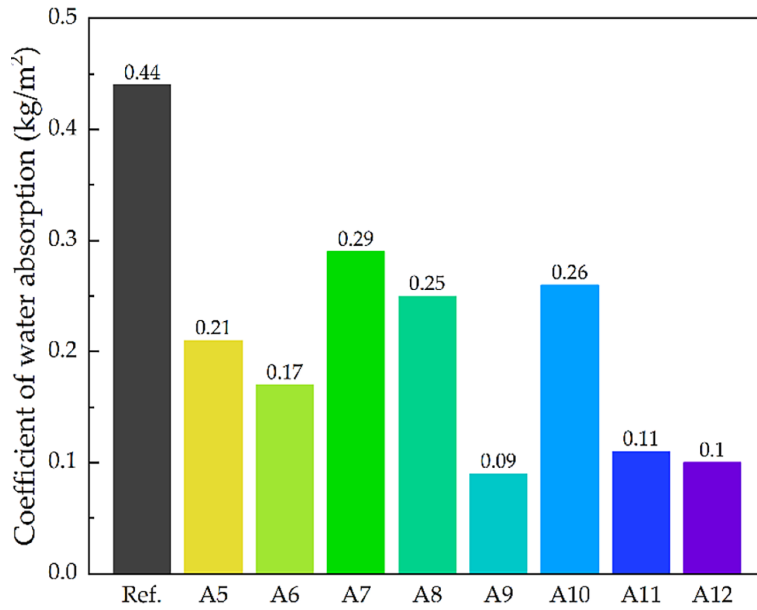


Figure 7. The water absorption coefficient caused by the rising capillary action

Frost resistance

Hydrophobized and standard concrete samples after conditioning in the laboratory were placed in a freezer and subjected to 50 cycles of freezing and thawing (F–T). One cycle lasted 8 hours (4 hours of freezing and 4 hours of thawing). Figure 9 shows selected samples after the frost resistance testing.

The determination of the frost resistance consisted of determining the percentage weight loss, according to the formula:

$$\Delta G = \frac{G_1 - G_2}{G_1} \cdot 100\% \quad (1)$$

where: ΔG – relative weight difference, %;
 G_1 – the average weight of the samples before their first freezing cycle, in a water-saturated state, kg;
 G_2 – the average weight of the samples after their last thawing cycle, in a water-saturated state, kg.

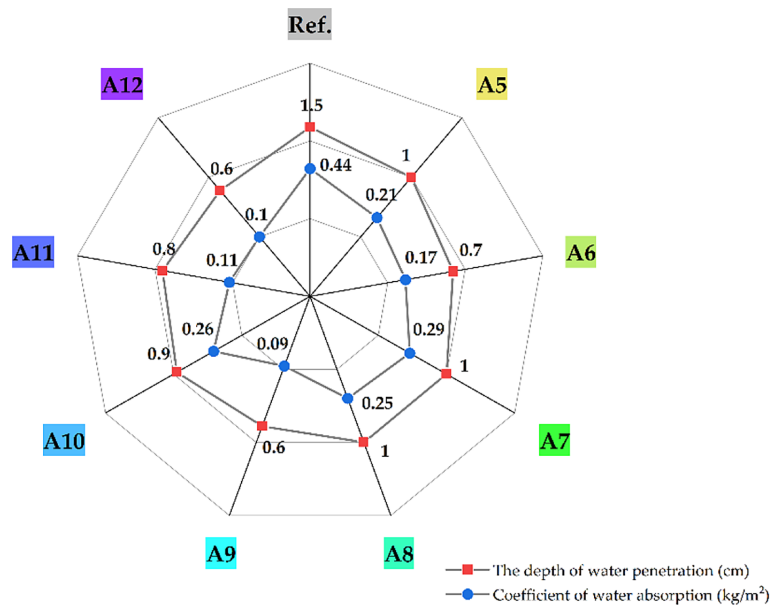


Figure 8. The water penetration depth into concrete samples during the water tightness test vs. water absorption coefficient caused by the capillary rising

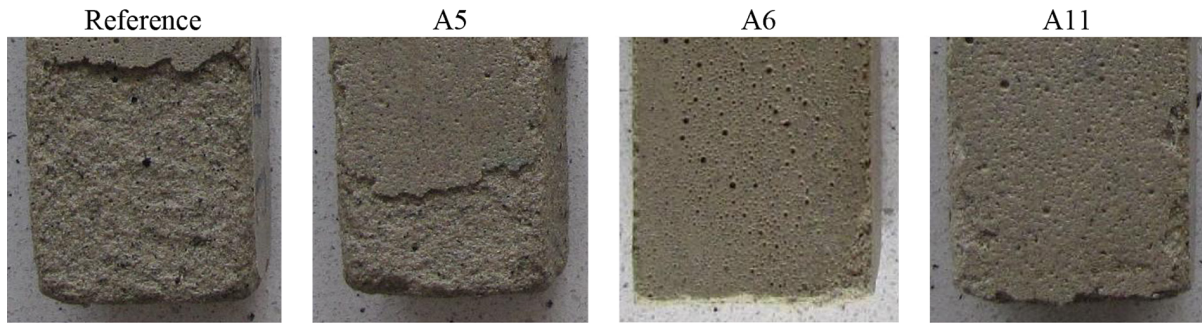


Figure 9. The condition of selected samples after 50 freezing and thawing (F–T) cycles

Figure 10 shows the frost resistance results. The state of preservation of the concrete samples after the hydrophobization is satisfactory. There is no visible damage, cracks, major deterioration, with the exception of the A5 formulation (see Fig. 9). The reference concrete showed a weight loss of 1.8%. In the case of hydrophobization, the weight loss was 33.3 to 72% less than the reference samples. The best effectiveness was demonstrated with formulations: A6, A8, and A9 which contain the Bioecobase and the Bioecobase-g in their composition and they were significantly better than the commercial A11 and A12 formulations. Szafraniec et al. [20] showed that the mortars subjected to the hydrophobization showed greater frost resistance. A weight loss was equal to 0.06–0.19% for the cyclic F-T, which is 11 to 34 times less weight loss than the reference mortars. Barnat-Hunek et al. [21] showed that after 25 F-T cycles there is marked improvement in the frost resistance of

concrete. In comparison to the reference samples, the weight loss was 86% lower. During the increased number of the F-T cycles, the pores are gradually merged, increasing the freezing pressure of water. For this reason, the speed of concrete destruction by freezing and thawing is accelerating. Hydrophobization prevents the rapid deterioration of concrete [45]. Shi et al. [45] indicated that a silanized rubber is beneficial to apply in a frost-resistant concrete mixtures to achieve parameters that ensure the frost resistance of concrete. At the optimal content of the hydrophobizing admixture in a concrete, a strong correlation is observed between the frost resistance and pores and voids structure. The effect of the hydrophobizing agents was studied by Wang et al. [46]. They found that thickness of frost layer on superhydrophobic surfaces decreased up to 30%. In addition, Kim et al. [47] studied a frost density and the lowest one was present on the hydrophobic surface.

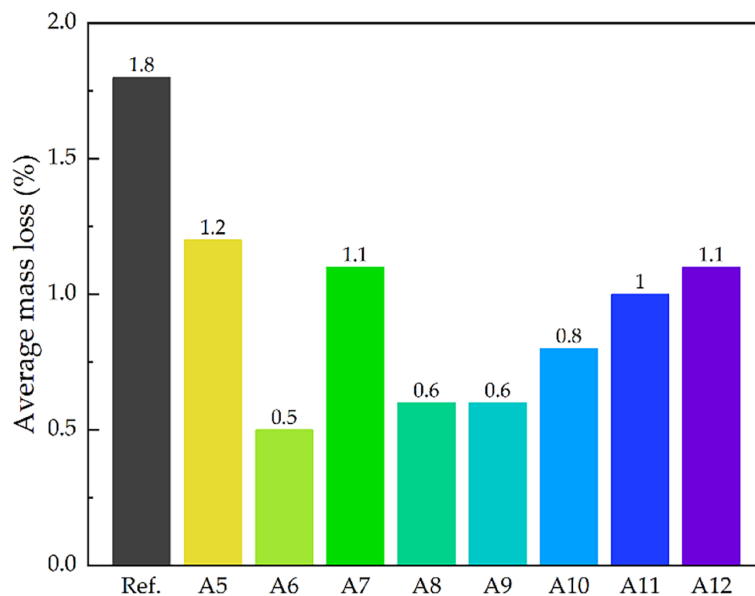


Figure 10. Average weight loss of concrete samples caused by the frost resistance test after 50 F–T cycles

Resistance to salts crystallization pressure

In this method, a 14% solution of the ten-hydrate sodium sulfate was used. According to the EN:12370 [33], 15 test cycles were carried out, after which the samples were washed under water and dried to a constant weight.

The salt crystallization resistance, that is, the difference in weight of the samples after the test, was calculated from the formula:

$$\Delta M = \frac{M_f - M_d}{M_d} \cdot 100\% \quad (2)$$

where: ΔM – relative weight difference before and after the test [%],

M_d – weight of the sample before testing [g],

M_f – sample weight after 15 test cycles [g].

Figure 11 shows the test results. The state of preservation of the samples after 15 test cycles and drying is shown in Figure 12.

In the case of hydrophobized concrete, the salt crystallization occurred inside the material structure. No damage except the A5 and A12 formulations (methylsilicone resin) was observed. The reference concrete was characterized by a lacked damage resistance caused by the crystallization of the ten-hydrate sodium sulfate. After 15 cycles the weight loss was 0.8%. Ibrahim et al. [48] proved that concrete applied to the silane surface hydrophobization is characterized by a total stability after immersion in a sulfate solution. In addition, Aguiar et al. [49] indicated that silicon protected concrete is characterized by a low performance. Sodium sulfate is very damaging because the subflorescence is highly to arise [43]. The damage caused by the sodium sulfate can be explained by two mechanisms: the pressure of hydration and crystallization [50,51]. Tsui et al. [52] showed that drying and soaking cycles in a salt solution, cause an extensive damage. It is caused by the precipitation of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$), which occurs when wetting process is applied and under the conditions in which the crystals are no longer allowed to grow in free directions.

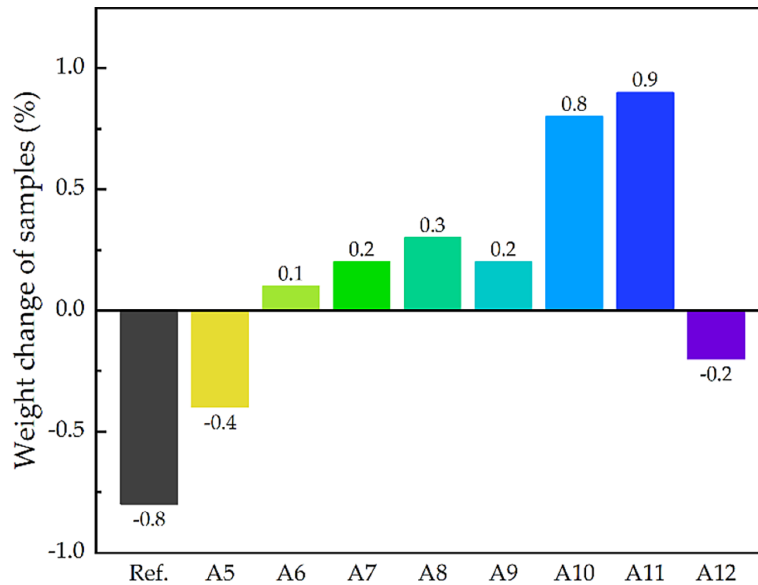


Figure 11. Weight change of concrete samples after 15 cycles of the salts crystallization

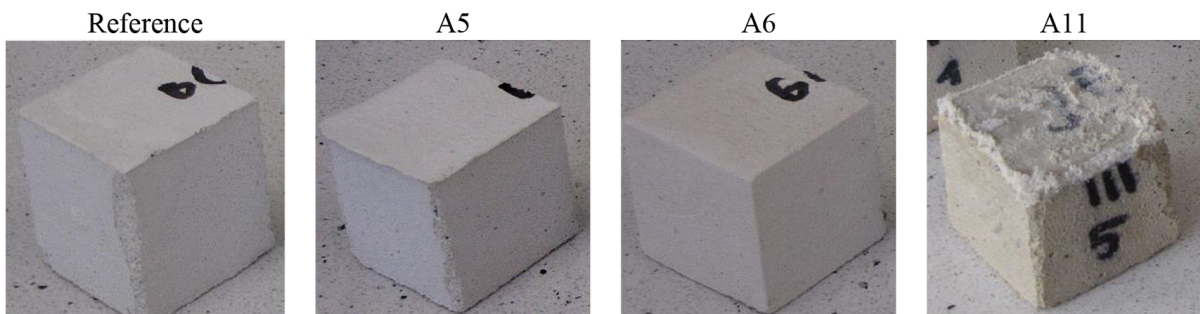


Figure 12. Selected samples and their state after 15 cycles of the salts crystallization pressure

As Suleiman et al. [40] showed in their study, the mechanism of protection with silanes differs from other coating materials studied by the authors because they chemically react in the concrete pores after diffusion through the concrete layer. This is accompanied by the supply of molecules that act as a hydrophobic agent, which was also confirmed by Vipulanandan et al. [53]. In our study, a protective film on the surface of concrete is provided by the higher fatty acids. This layer can be hardly damaged by sulfates, thus reducing the rising of salt solutions by capillaries in concrete. On the other hand, poor protection of the surface from the aggressive effects of sulfates was obtained by the methyl silicone resin (A12). However, the water-repellent A9 agent, which contains higher fatty acids and a methyl silicone resin, no longer caused a loss of weight in the concrete specimens, but a slight increase.

CONCLUSIONS

The tests performed indicated that higher fatty acids of vegetable oils origin can be applied as a component of concrete hydrophobizing agents, meeting the standard requirements for such agents. These preparations are characterized by a good functional properties and high hydrophobization efficiency.

The products based on the Bioecobase are characterized by densities lower than 1.0 g/cm^3 while the water-soluble formulations showed densities greater than 1.0 g/cm^3 . The viscosity coefficient η showed that the agent A11 had the lowest dynamic viscosity, while the agents A5 and A9 with the Bioecobase and methyl silicone resin had the highest dynamic viscosity ($0.045 \text{ Pa}\cdot\text{s}$). The aerobic biodegradability calculated as the BOD/COD ratio for the Bioecobase was equal to 95.1%. The agents based on the nanosilane (A6, A8, A10, A11) and on the methyl silicone resin (A12) made the concrete surface to be superhydrophobic ($CA > 120^\circ$). The decrease in concrete water absorption after using A5-A10 formulations ranged from 52.5% to 75%. It was observed that very good concrete hydrophobization efficiency. The vapor permeability test showed that water repellents increased the coefficient of vapor diffusion resistance, with the vegetable oil-based formulation (Bioecobase) and methylsilicone resin in organic solvent (A9) caused the greatest sealing, followed by the water agent A6 (33.3% nanosilane; 33.3% water; 33.3% Bioecobase-g).

The A6 formulation reduced the water rise in concrete by more than two times. The water tightness class was determined to be W8. The Bioecobase-based formulations showed greater blockage to water. The best result was obtained for the A9 agent (0.6 cm) and the commercial A12 formulation. In the case of hydrophobization, the weight loss after frost test was 33.3 to 72% less than the reference samples. The best effectiveness was demonstrated with formulations: A6, A8, and A9 which contain the Bioecobase and the Bioecobase-g. In the case of hydrophobized concrete, the salt crystallization occurred inside the structure of the material without causing any damage except in the case of the A5 and A12 formulations (methylsilicone resin). The reference concrete is not resistant to damage caused by the crystallization of the ten-hydrate sodium sulfate, the weight loss in this case was 0.8% during 15 test cycles.

Very good properties were achieved despite the use of vegetable waste – natural oils. This is extremely important due to the ecological aspect associated with the disposal of the waste. In addition, an agent with a high degree of environmental performance was obtained, as the volatile organic compounds (VOCs), which are contained in methylsilicone resin in aliphatic hydrocarbon solvent, were largely replaced by the biodegradable Bioecobase derived from vegetable natural oils. Aqueous formulations (A6, A10) are characterized by ecotoxicological properties and they reducing the environmental impact of volatile organic compounds (VOCs), as they consist exclusively of biodegradable components.

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