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Influence of hydrophobisation on surface free energy of hybrid fiber reinforced ultra-high performance concrete

Danuta Barnat-Hunek [a], Piotr Smarzewski [b,*]

[a] Lublin University of Technology, Faculty of Civil Engineering and Architecture, Department of Construction, Nadbystrzycka St. 40, 20-618 Lublin, Poland
[b] Lublin University of Technology, Faculty of Civil Engineering and Architecture, Department of Structural Engineering, Nadbystrzycka St. 40, 20-618 Lublin, Poland

HIGHLIGHTS

- The content of fibers increases adhesion of the hydrophobic agents on the ultra-high performance concrete (UHPC) surface.
- The highest hydrophobisation efficiency of the FRUHPC was obtained by a alkyl–alkoxy-silanes.
- The SFE is nonlinear dependent on the UHPC absorptivity.
- The strong correlations between the SFE values and the contact angle were formulated.
- The Neumann and Owens–Wendt methods gave the most reliable SFE results.

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ABSTRACT

The aim of the research presented in the paper was to evaluate the feasibility of using hydrophobic preparations based on organosilicon compounds for protection treatment on the hybrid fiber reinforced ultra-high performance concrete (FRUHPC) surface. Three polisiloxanes agents were deposited onto the seven types of concretes, with a steel-polypropylene fiber content ranging from 0% to 1%. In this investigation, the surface free energy (SFE) of the coatings was calculated using the Owens–Wendt, Neumann, Wu, and Fowkes methods. In order to examine the contact angle, three measuring liquids were used: distilled water, glycerine and diiodomethane. It has been shown that the Neumann method with one polar and the Owens–Wendt method with a pair of polar liquids gave the most reliable results.

1. Introduction

Ultra-high performance concrete (UHPC) is a type of structural concrete with a compressive strength above 120 MPa and very high durability. The material is characterized by high strength, low absorbability, low water permeability and high freeze resistance, which results in high durability [1]. Fibers are added to the matrix as reinforcement to control cracking and to improve the general ductility of the material [2]. Some properties of concrete can be improved by polypropylene or steel fibers. Usually, in order to improve the mechanical and physical properties, especially tensile and flexural strength as well as long-term concrete shrinkage, steel fibers are used. On the other side, polypropylene fibers do not corrode, are thermally stable, chemically inert and very stable in the alkaline environment of concrete [3,4]. Moreover, the polypropylene has a hydrophobic surface (does not absorb water) and it does not interfere in the concrete hydration reaction [5].

UHPC are often exposed to aggressive impacts of the environment and therefore they must have a high resistance to chemical corrosion, frost corrosion, weathering, impact of aggressive water and many other corrosive agents. One of the methods used to protect the concrete surface from corrosion caused by moisture is hydrophobisation [6]. Organosilicon compounds – siloxanes or methyl silicone resins [7,8] are mostly used as concrete hydrophobising agents. The wettability of concrete by means of liquids which contain corrosive components is of great importance in practice. It may indicate the adhesive properties of concrete, as well as protective coatings applied to its surface.

Some treatments previously reported in literature for fibers in concrete applications include plasma based treatment [9], acid and other chemical treatments [3,10], are able to modify the fiber and concrete, changing the roughness, and polarity of the surface [11].

* Corresponding author.
E-mail address: p.smarzewski@pollub.pl (P. Smarzewski).

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The research on the cement mixes and the concrete properties, including their wettability and SFE, are considered to be important elements in assessing adhesion properties. The surface free energies and their components between two interacting surfaces are extremely important since not only do they dictate the strength of interaction, but also control processes like the stability of aqueous colloidal suspensions, wetting, spreading and adhesion [12–14].

The contact angle of materials is an indicator of their wettability properties. High wettability – hydrophilicity occurs at a low contact angle – less than 90°, and insufficient wettability – hydrophobicity at a high contact angle – more than 90°. The contact angle can be used to determine surface tension, and to define surface free energy [15,16].

The highest decrease in SFE can be due to coatings which hydrophobise the surface to the greatest extent. SFE depends on the chemical reactivity of the silanes used, the type of solvent, the viscosity and surface tension of the solution. SFE represents the state of imbalance of intermolecular interactions present at the phase boundary of two different mediums. There are numerous methods to directly determine the SFE of liquids.

Selecting the method for calculating SFE is important. The methods of using a pair of liquids gave results depending on the type of liquid. In the literature contact angle studies of building materials by using diiodomethane, mercury, nonpolar aprotic: hexadecane, dodecane, decane and hexane and polar protic: deionized water, glycerol, formamide, ethylene glycol, diacetone alcohol, α-bromonaftalen, toluene can be found [17–19].

The Owens–Wendt method is commonly used to determine the SFE of materials. In this investigation, the SFE of the coatings were calculated using the Owens–Wendt, Neumann, Wu, and Fowkes methods.

The chemical agents, polisiloxanes, were used to modify the surface properties of FRUHPC, making it more hydrophobic and, therefore, unable to be wetted by water. In cases where significant resistance of the concrete surface layer to the impact of corrosive environments is required, it is desirable to use preparations with the lowest SFE value.

2. Experimental procedure

2.1. Materials

The following components were used in the recipes of the seven concrete mixtures: Portland cement CEM I 52.5 N-HSR/NA – 670.5 kg/m^3, coarse aggregates – granodiorite 2/8 mm or granite 2/8 mm–990 kg/m^3, quartz sand 0/2 mm–500 kg/m^3, water – 178 l/m^3, silica fume – 74.5 kg/m^3, superplasticizer – 20 l/m^3, as well as quantities of steel and polypropylene fibers. Determination of the particle size distribution for the aggregate and sand were performed based on Standard EN 933-1:2000. In order to attain the same workability, a superplasticizer based on polycarboxylate ethers was used in the concrete mixtures. In the first three concretes – granodiorite aggregate was used, and in the remaining four – granite aggregate. The detailed characteristics of the fibers are shown in Table 1.

The mixtures were prepared using a concrete mixer with a capacity of 100 l. Concrete samples were made based on the recipe determined experimentally using known mortar by EN 206:2014-04. The quartz sand and coarse aggregate were homogenized together and mixed with half the quantity of water. Then, the cement, silica fume and the remaining water were added and finally the superplasticizer. The components were thoroughly mixed. The steel and polypropylene fibers were gradually added to obtain a homogeneous and workable consistency. The fibers were dosed gradually so as not to clump or sink to the bottom of the mixture. Samples were formed directly after the concrete compounds were mixed according to EN 12390-2:2011. In Table 2 the abbreviated concrete types and quantities of steel and polypropylene fibers for various batches are shown.

Moulds coated with an anti-adhesive substance were filled with the concrete mixtures and compacted on a vibrating table. All the samples were stored at a temperature of about 23 °C until removing them from the moulds after 24 h and they were then placed in a water tank for 7 days to cure. After 7 days the samples were removed from the tank to cure in laboratory conditions to up to 28 days.

Table 1
Detailed characteristics of fibers.

Type of fiber	Density (g/cm^3)	Length (mm)	Diameter (μm)	Elastic modulus (GPa)
Steel fiber, ST	7.8	50	1000	200
Polypropylene fiber, PP	0.9	12	25	3.5

2.2. Experimental techniques

2.2.1. Physical and mechanical properties of concrete

2.2.1.1. Physical properties. Tests of apparent density were performed in accordance with PN-EN 12390-7:2001. Three cubic samples of 100 × 100 × 100 mm from each batch were used.

The absorptivity test was performed on cubic specimens in accordance with Standard BS 1881-122, 2011. The specimens were cured in water at 22 °C. The specimens were dried in an oven at 45 °C for at least 14 days. In the case where the difference between values obtained from two successive measurements of mass exceeded 0.5% of the lesser value, the specimens were returned to the oven for an additional 24-h drying period. Weights of the specimens were then measured at additional days until the difference between any two successive measurements was less than 0.5%. The cured specimens were then immersed in the water tank for 1, 3, 7, 14 days and they were weighed on a 0.01 g balance after being wiped with a dry paper towel.

2.2.1.2. Compressive strength, splitting tensile strength, modulus of elasticity. Cubic concrete samples with the following dimensions: 100 × 100 × 100 mm were applied. Research was conducted according to EN 12390-3:2002 normative – compressive strength and EN 12390-6:2001 normative – splitting tensile strength. Evaluation of the concrete grade was elaborated using a servo-hydraulic closed-loop test machine within 3 MN after 28 days of maturation, when the average compressive and splitting tensile strengths were obtained by the samples (Fig. 1).

Determination of the modulus of elasticity was carried out on cylinders of 150 mm in diameter and a height of 300 mm by measuring the deformation of the sample in the stress range from 0.5 MPa to 30% of the concrete compressive strength. The examination was conducted by means of a press and using a modulus measuring device with an extensometer according to the recommendations of ASTM C 469-02:2004.

2.2.2. Hydrophobic materials

Three hydrophobic preparations were selected for laboratory tests, commonly used in construction chemicals which differed in the type of solvent, viscosity and concentration:

P1 – water - based solution of methyl silicone resin in potassium hydroxide (1:6),

P2 – organic solvent based on alkyl–alkoxy-silanes oligomers,

P3 – organic solvent based methyl silicone resins (MESI) are macromolecular compounds.

Alkyl–alkoxy-silanes are reactive compounds of silicone and organic nonpolar functional groups R–Si–(OR')$_3$. The impregnation efficiency is determined mostly by the chemical composition of the monomers: the alkoxy groups (OR') determine the reactivity of the compound and the alkyl groups (R) define the hydrophobic efficiency of the impregnated material.

Each concrete was sliced into twelve equal parts. Then the samples were dried at 70 ± 5 °C until a solid mass was obtained. Three samples were impregnated with each of the hydrophobic agents and another three samples were taken as reference, which were used for comparative purposes. Two layers of the preparation were applied, using a brush. Agent P1 was diluted in the following proportions – 1:6 according to the manufacturer's requirements. The other hydrophobic preparations

Table 2
Percentage of fibers in various concretes.

Type of concrete	Percentage (%)		Mass (kg/m^3)	
	Steel fibers ST	Polypropylene fibers PP	Steel fibers ST	Polypropylene fibers PP
C1	–	–	–	–
FC1	1	–	78	–
FC2	0.75	0.25	58.5	2.25
FC3	0.5	0.5	39	4.5
FC4	0.25	0.75	19.5	6.75
FC5	–	1	–	9
C2	–	–	–	–