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Microstructural investigations on the skinning of ultra-high performance concrete

Alexander Wetzel *, Christoph Glotzbach, Kasem Maryamh, Bernhard Middendorf

University of Kassel, Faculty of Civil and Environmental Engineering, Institute for Structural Engineering, Dept. of Structural Materials and Construction Chemistry, Germany

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ABSTRACT

A skinning phenomenon occurring in the first seconds to minutes on ultra-high performance concrete (UHPC) was analysed by microstructural investigations. The low water content and the resulting high content of superplasticizers, i.e. polycarboxylate ethers, lead to differences in rheological behaviour of fine grained UHPC containing silica fume. A visco-elastic surface layer impedes the deaeration and constrains smoothing of the concrete surface. A detailed multi-method characterization of the microstructure of the layered cross-section revealed enrichments of polycarboxylate ether superplasticizers (PCE) on the surface of the UHPC. FITC-staining of the PCE made a localisation and relative quantification possible. A hypothesis for the formation of the skin comprising PCE enrichment driven by evaporation is derived from this microstructural study.

1. Introduction

On the surface of ultra-high performance concretes (UHPC) and self-compacting concretes, a phenomenon that has been colloquially described as "elephant skin" can be observed seconds to minutes after casting. This skin induces disadvantages at the fresh and hardened state. Although it is known that the formation of this skin can be prevented for instance by curing with water vapour, the mechanisms of formation of this skin have not been discussed in detail in literature yet.

The high strength and durability of ultra-high performance concrete is owed to its high packing density, which is gained by optimized composition of fines as silica fume and quartz powder and the low water/binder ratio of $\leqslant$0.20 [1]. Both the increase of the specific surface of the additives and the decrease of the water/cement ratio necessitate the use of high performance superplasticizers in order to ensure a good workability of the fresh concrete. The surface layer, which will be referred to by its colloquial name "elephant skin" in the following text, usually forms on fresh UHPC in a span of only 30 s up to several minutes after casting. It develops at low relative humidity (RH), while at higher RH skin formation is prevented [2]. The possibility of smoothing the concrete surface is limited by the visco-elastic behaviour of this skin (Fig. 1). Due to this visco-elastic behaviour, the elephant skin wrinkles as a consequence of pulling out the tip of a screwdriver, for example.

Another effect resulting from the skin formation is the reduction of deaeration of the fresh mortar or concrete. This was found in studies concerning the deaeration in relation to varying content of fines, superplasticizer or water/binder ratio [3]. The formation of elephant skin is not restricted to fine grained formulations, but can also be observed on UHPC with coarse aggregates (e.g. for a formulation given in [4]).

In terms of crack formation and evolution of cracks, Dehn [5] as well as Scheydt et al. [6] already studied the phenomenon of elephant skin formation. They explained the formation with a bleeding effect. The formation of this skin is hampered under high relative humidity, as will be shown in this contribution. Thus, the sedimentation as the main driving force can be neglected. As already mention above, the skin is a phenomenon which was observed on UHPC and self compacting concrete (SCC), promoting the assumption that formation of elephant skin is related to an increased content of fines and/or a high content or the mode of action of superplasticizers, i.e. the polycarboxylate ethers (PCE).

Chemical admixtures used in mortars and concretes such as superplasticizers are difficult to identify and quantify by conventional methods due to (i) dissolution and/or mobilization during preparation and (ii) resolution constraints of conventional analysis methods. A method which was developed by Jenni et al. [7] and used elsewhere [8,9] was therefore adapted and modified. The superplasticizer used in present studies was marked with a

* Corresponding author. Tel.: +49 561 804 2603; fax: +49 561 804 2662.
E-mail address: alexander.wetzel@uni-kassel.de (A. Wetzel).

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fluorescent dye (fluorescein isothiocyanate, FITC). The functionalized polymer was then localised and quantified relatively by laser scanning microscopy (LSM) on a polished cross section of a fine grained mortar, which corresponds to the fraction <125 μm of a specific mixture which was used in several studies concerning UHPC [10].

Combined with other microstructural investigations, the elephant skin was characterized in detail resulting in a hypothesis for a skin formation mechanism. According to this hypothesis, the skin is formed by a combined process of drying and film formation as a consequence of enrichments of superplasticizers.

2. Methods

2.1. Sample mixture

In order to suppress the multitude of possible influencing factors, a simple fine grained mortar mixture based on an UHPC mix [10] was chosen for this investigation (Table 1). The polycarboxylate ether used in these investigations is of MPEG-type with a molecular weight of approximately 20,000 g/mol (Fig. 2). The mortar formulation has been analysed in a former research project in terms of deaeration properties, and a strong tendency for the formation of the elephant skin was observed [3].

The mortar contains fine aggregates (quartz powder), finest additives (silica fume) and superplasticizers on the basis of polycarboxylate ether. In preliminary tests, three different commercial PCEs were compared to estimate the influence of different superplasticizer on the formation of the skin. However, no notable difference in the resulting flowability was found, and in all cases, skinning occurred in a comparable amount. The superplasticizer needs some time to develop its full efficiency, therefore a certain mixing procedure with high mixing energy is necessary for UHPC formulations with a very low water/cement-ratio [11]. Within these investigations, only small amounts of mortar were mixed using an intensive mixer with a special mixing program lasting 15 min in total.

2.2. Sample preparation

The mortar was cast into formworks ($4 \times 4 \times 16\ cm^3$) made of steel or polystyrene directly after mixing. The samples were separated into groups, each cured at different relative humidities, but all at a constant temperature of 20 °C: In a water vapour saturated exsiccator, a RH >95% was realized, while 60% RH was achieved in a climate chamber. Additionally, some samples were stored in 30% RH The mortar surfaces were refreshed by stirring after the samples had been placed in controlled environments. After 24 h, the samples were all stored under standard climate conditions (20 °C, 60% RH). After seven days, the samples were cut into pieces

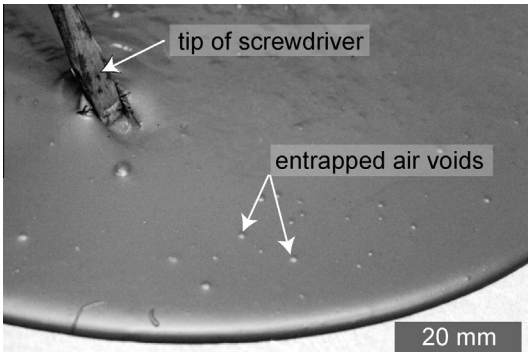

Fig. 1. Surface of UHPC mortar showing elephant skin with plastic behaviour.

Table 1
Formulation of UHPC mortar.

Component	Weight [%]
CEM I 52,5 R HS-NA	69.99
Silica fume	11.66
Quartz powder	16.31
Superplasticizer (PCE)	2.027
Water	12.98
Water/cement ratio: 0.20	

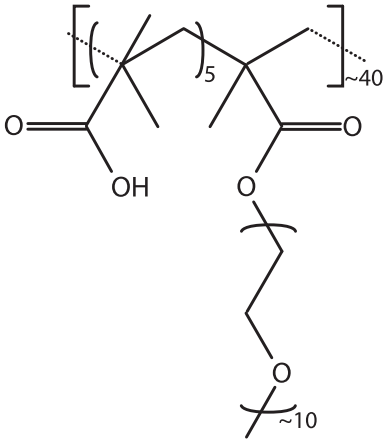

Fig. 2. Structure of the used superplasticizer polymer.

of $4 \times 4 \times 1\ cm^3$. From these slices, polished cross-sections, thin-sections and fractured faces (cross-section) were prepared this way for further microstructural investigations. The polished cross-sections were produced with a cold-hardening 2-component epoxy resin and ground and polished in several steps with 3 μm diamond suspension as a final step. Thin-sections were prepared with a thickness of approx. 20 μm and polished in a final step with 1 μm diamond suspension and were not covered by a cover glass. Furthermore, slices were divided along the vertical axis by a precision saw yielding sample slices representing different depths below the mortar surface. These slices afterwards were analysed by X-ray powder diffraction (Bruker D4) and mercury intrusion porosimetry (Quantachrome).

2.3. Microindentation

The distribution of the hardness on a polished cross section was quantified by microindentation using a method common in metallography [12]. While a Vickers pyramid is penetrating the cross sections surface under a defined velocity, the ratio of maximum force to contact area is monitored and yields the universal hardness in N/mm^2. With a measuring grid of 30×30 measuring points, an area of 1000×1000 μm was analysed.

2.4. Functionalization of PCE

Beside its wide availability, FITC was chosen as fluorescent dye as its stability in the harsh conditions of construction materials has already been established [7,9]. However, the described reactions lead to a very low yield. Thus, to ensure a stable bond to the PCE molecules, a better binding site was to be introduced first.

30 ml PCE solution (containing 12.9 g of active agent, ~0.7 mmol) were dried in a vacuum chamber (~0.2 mbar, 20 °C), resulting in a solid residue. The educt was then heated under reflux (~30 mbar) in 70 ml toluene at 65 °C for about 2 h, until it was