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DOI
10.1007/978-3-031-15805-6_14

Publication date
2023

Document Version
Final published version

Published in
Strain Hardening Cementitious Composites

Citation (APA)
He, S., Liang, M., Yang, E., & Schlangen, E. (2023). A New Method to Quantitatively Characterize the Porosity of Fiber/Matrix Interfacial Transition Zone (ITZ) via Longitudinal Cross-Sections. In *Strain Hardening Cementitious Composites: SHCC5* (1 ed., Vol. 39, pp. 127-134). (RILEM Bookseries; Vol. 39). Springer. https://doi.org/10.1007/978-3-031-15805-6_14

A New Method to Quantitatively Characterize the Porosity of Fiber/Matrix Interfacial Transition Zone (ITZ) via Longitudinal Cross-Sections

Shan He[1(✉)], Minfei Liang[1], En-hua Yang[2], and Erik Schlangen[1]

[1] Microlab, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft 2628 CN, The Netherlands
s.he-2@tudelft.nl

[2] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639797, Singapore

Abstract. The properties of the interfacial transition zone (ITZ) between microfiber and cement-based matrix are of primary significance for the overall behavior of strain hardening cementitious composites (SHCCs). However, due to the relatively small diameter of polymeric microfibers (e.g., PVA fiber), it is technically difficult to obtain quantitative and representative information of the properties of the ITZ. In the current study, a new method that is able to quantitatively characterize the microstructural features of the ITZ surrounding a well-aligned microfiber was reported. With the method, the porosity gradients within the ITZs between PVA fiber and cement paste matrices with different water to cement (w/c) ratios were determined. The results show that the matrix surrounding a microfiber were more porous than the bulk matrix. The thickness of this porous region can extend up to 100 microns away from the fiber surface even at a relatively low water to cement ratio (w/c = 0.3). It is thus believed that the method could facilitate the investigation and modification of fiber/matrix bond properties and also contribute to the development of SHCC with superior properties.

Keywords: ITZ · Porosity · Image analysis · Fiber

1 Introduction

The interfacial transition zone (ITZ) between an inclusion (e.g., aggregate) and bulk matrix in cement-based composites has been the focus of extensive research. Now it is well accepted and documented that the ITZ is quite different in its microstructure, composition and mechanical properties than the bulk cement matrix as a result of the disruption created by the inclusion to the packing of its surrounding cement particles [1, 2]. Because of the loose packing, the ITZ is usually more porous and weaker compared to the bulk matrix, and in many cases governs the mechanical properties and durability of cement-based materials. This phenomenon is usually addressed as the "wall" effect

M. Kunieda et al. (Eds.): SHCC 2022, RILEM Bookseries 39, pp. 127–134, 2023.
https://doi.org/10.1007/978-3-031-15805-6_14

[3, 4]. It is believed that as long as an inclusion is sufficiently large to act as a wall against the cement particles, an ITZ will form around the inclusion.

The question arises as to whether an ITZ will form around a microfiber that has only one dimension (length) being much larger than cement particles, while its another dimension (diameter) is of the same order of magnitude as that of the cement grains. Previous studies on the characterization of the ITZ between microfibers and cement paste also reported contradictory results. Based on scanning electron microscopy (SEM) examination, it has been reported that microstructure of interface between microfiber and cement matrix is dense and no obvious ITZ can be observed, which differs from that around bigger inclusion, such as aggregates and macro-fibers [5]. This has been attributed to the fact that diameter of microfibers is of the same order of magnitude as that of cement particles, and thus the wall effect that gives rise to the formation of ITZ may be largely minimized. However, Chan and Li [6] reported that porous structure were observed around a polyethylene fiber with a diameter of 38 μm in cement paste and showed that the porosity decreases when the water-to-cement ratio (w/c) is reduced. Recently, He et al. [7, 8] reported that porous ITZ could still be observed even when the w/c of the matrix is as low as 0.2.

We argue that disagreement among published literatures on the subject matter may be due to 2 reasons. Firstly, microstructural observation made by SEM is qualitative by nature. It is possible to compare 2 microstructures and decide which one contains more pores. But determining whether a microstructure is porous or not would be largely subjective. Secondly, established methods for studying the ITZ around a fiber often perform analyses on cross-sectional planes that are either perpendicular or intersect with the fiber axis at a random angle. This way of analysis can lead to errors and uncertainties for that the microstructure of the ITZ could be quite different from place to place due to the heterogeneity along its longitudinal direction.

To address the issues mentioned above, this paper reports a new method to quantitatively characterize the ITZ between microfiber and cement matrix. Instead of analyzing the porosity of ITZ on sections perpendicular to the fiber axis, we prepared longitudinal section passing through the central axis of the fiber for ITZ characterization by backscattered electron (BSE) imaging. With the method, the porosity gradients within the ITZs between PVA fiber and cement paste matrices with different water to cement (w/c) ratios were determined.

2 Materials and Methods

2.1 Materials

In this study, CEM I 42.5N Portland cement was used to prepare cement pastes with varying water to cement (w/c) ratio from 0.3 to 0.5. The microfiber used to produce the ITZ is a PVA microfiber with a diameter of 39 μm. Table 1 summarize the physical properties and geometry of the PVA fiber used in this study. All the specimens were cured in a climate room (20 °C and ≥ 98% RH) and have an age of 14 days on the day of analysis.

Table 1. Physical and mechanical properties of PVA fibers.

Diameter (μm)	Density (kg/m3)	Nominal tensile strength (MPa)	Young's modulus (GPa)	Surface oil-content (wt.%)
39	1300	1640	41.1	1.2

2.2 Detailed Sample Preparation Method

In the current study, characterization of the porosity follows the well-established method of quantitative backscattered electron (BSE) image analysis [9], which usually comprises: 1) section a specimen to expose the targeted microstructure; 2) use epoxy resin to impregnate the pores; 3) grind away excessive epoxy on the surface and polish the section; 4) examine the polished section under BSE; and 5) BSE image analysis. The challenge of applying this method to characterize the ITZ surrounding a microfiber lies on making a well-controlled cut near the fiber. This is because that only by making a cut as close and parallel to the embedded fiber as possible can the pores of the ITZ be exposed. As the diameter of a microfiber is only several tens of microns, the positional accuracy of the cutting need to be at micron level. For this reason, in the current study we adopted an automatic dicing machine, which is originally used in the semiconductor industry to perform cutting of silicon wafers. A detailed sample preparation procedure is given below.

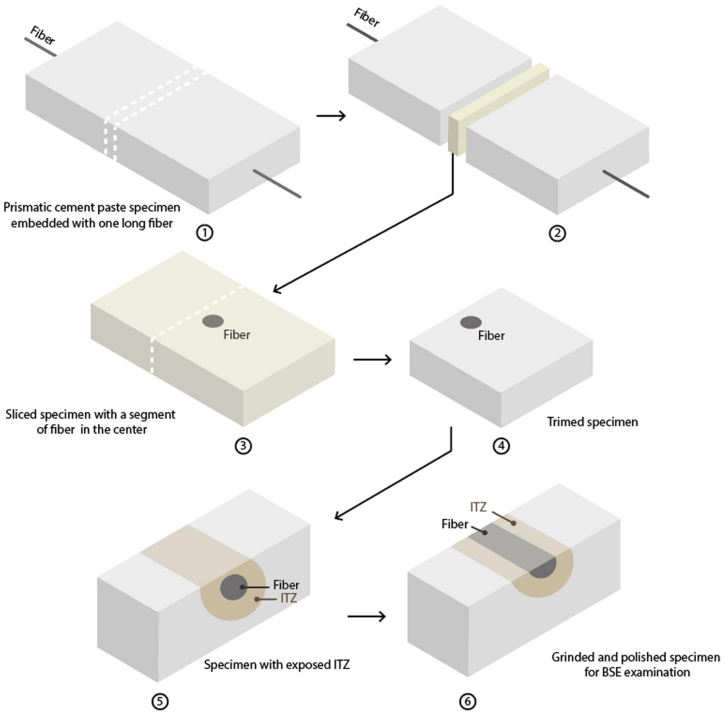

Fig. 1. Schematic illustrations of the sample preparation procedure.

Figure 1 illustrates the main step of preparation procedure. To prepare the specimen, a long PVA fiber was first cut into about 150 mm in length and fixed at the center of a prismatic mold, which will then be filled with fresh cement paste on a vibration table. After demolding, the cement paste prism embedded with one continuous fiber was sliced into thin plate-like specimens with the help of a diamond saw. The thickness of the specimens is between 1 to 2 mm. Each resulting specimens would have a segment of fiber embedded in the center perpendicular to the base surface. The position of the fiber was then identified with the use of an optical microscope and a precise cut was made by a dicing saw roughly 10 microns away from the fiber. Right after the cutting, the specimens were impregnated with epoxy resin and cured in an oven at 40 °C for 24 h. Figure 2 shows the fluorescence and electron microscope images of the specimen after epoxy impregnation. As can be seen, the epoxy successfully impregnated into the pores and a relatively wide porous region can be observed in the middle of the images.

The next step of the preparation is the progressive grinding of the specimen from the cutting plane to remove excessive epoxy and to expose the ITZ. The grinding was stopped exactly at the moment when the grinding surface reaches the center of the fiber. This is to avoid having an angled slice which may lead to exaggerated measurement of the ITZ thickness. The last step is to carefully polish the surface for optimum imaging under the BSE. The grinding and polishing were performed by using an in-house designed system. The details of the set-up can be found in a previous publication by the authors [8].

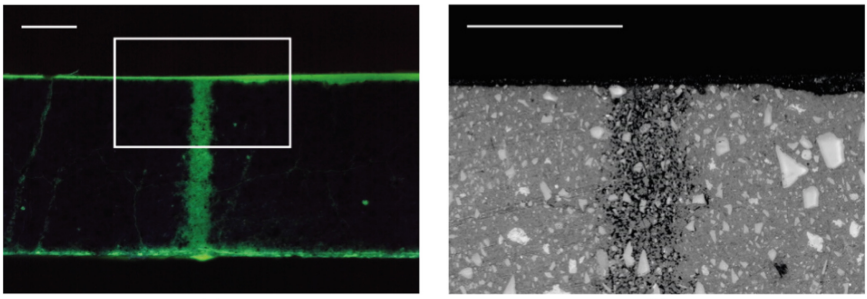

Fig. 2. Fluorescence light micrograph and scanning electron micrograph of the specimen after epoxy impregnation (scale bar = 500 μm)

The polished samples were examined under the BSE detector in an environmental scanning electron microscope (ESEM) at a voltage of 15 kV without coating. Figure 3a shows a typical BSE image of specimen with polished surface, which was made by digitally stitching 8 individual images taken at a magnification of ×500 (1 pixel = 0.3 micron). Contrast in the BSE image yields clear definition of constituents, e.g., the region in light grey corresponds to the anhydrous cement while regions in black resembles pores. Figure 3b shows the binary image with white pixels representing the pores after segmentation. The porosity gradient of the ITZ was then calculated by counting the fraction of white pixels to all pixels in each horizontal lines from the fiber surface. At least 2 specimens were examined for each water to cement ratio.

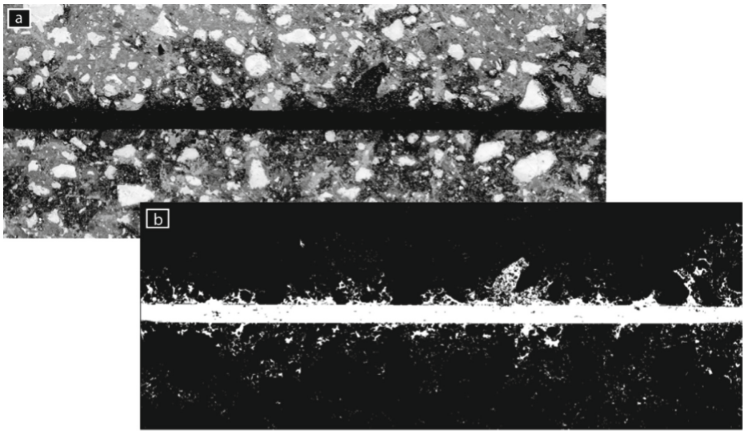

Fig. 3. (a) Typical BSE image of a polished specimen and (b) binary image converted from the BSE image (length of embedded fiber = 2.5 mm).

3 Results and Discussion

3.1 Porosity Gradient

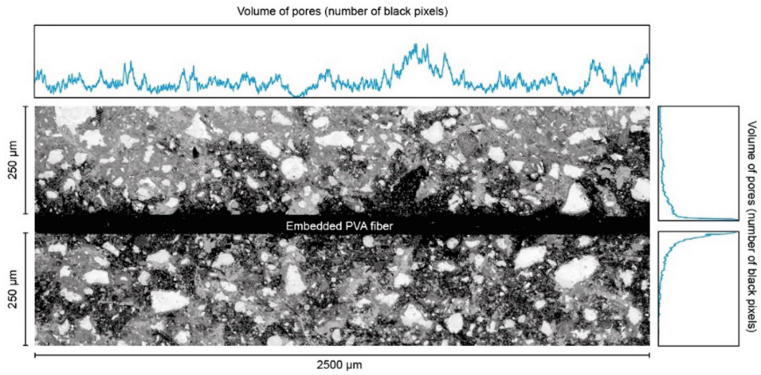

Fig. 4. BSE image of a polished ITZ specimen.

Figure 4 shows a typical stitched BSE image of a longitudinal section of the ITZ surrounding a microfiber, in which anhydrous cement and hydrated phase can be distinguished on the basis of their grey level. The fiber can be easily identified in the middle of the graph as a black rectangular for that PVA fiber contains mainly the element of carbon and therefore appears as dark black under BSE. Also in black color, epoxy filled pores in the size of several tens of micron could be seen in the vicinity of the fiber. The line figures above and next to the BSE image shows the number of black pixels per each vertical and horizontal lines, respectively, representing the change of the volume of the pores along the longitudinal and radial directions. As can be seen form the figure on the right of the BSE image, the zone in the vicinity of the fiber contains a much higher number of pores

as compared to the bulk matrix far away from the fiber, suggests existence of a porous transition zone between micro-fiber and cement matrix. Furthermore, from the figure about the BSE image, it can be found that porosity in the ITZ is not homogeneous along the length direction of the fiber. Concentration of pores can be seen at some locations, while some areas remain dense. This reveals that the ITZ between microfiber and cement paste is highly heterogenous along its length direction. As a result, existing ITZ analysis methods performed on sections intersecting with fiber at a random angle can lead to errors and uncertainties.

Figure 5 shows the porosity gradient in the ITZ for different w/c ratios based on the BSE imaging analysis. As can be seen, for all the groups the porosity within 5–100 μm is significantly higher than the bulk matrix. Volume fraction of pores decreases with increasing distance from fiber/matrix interface. The reduction rate is high within 5–50 μm from the interface and turns into moderate beyond 50 μm. This suggest that the microstructure of the hydrated cement paste is highly modified in the vicinity of microfibers for all the tested w/c ratios. The porous zone can extend up to 100 μm from the interface into the matrix with the most porous region being in the region of within 50 μm adjacent to the fiber. Surprisingly, the porosity gradient was found not to be influenced by the w/c ratios. This may be because the age of the specimens used in the current study is only 14 days. It is possible the effect of w/c may be more pronounced when the hydration degree is higher. It should be noted that in Fig. 5 the porosity measurement starts from 5 microns away from fiber surface but not from the exact physical fiber/matrix interface. This is because we consider our measurement of

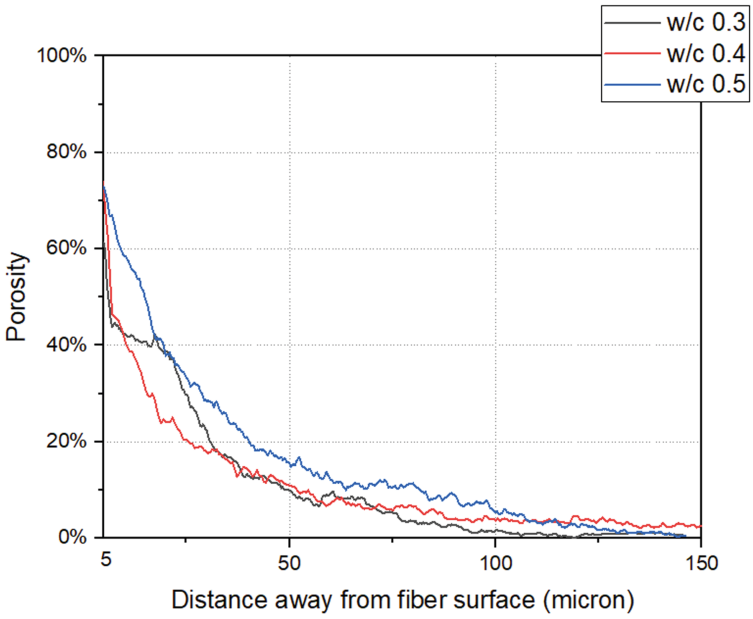

Fig. 5. Volume fraction of pores at different distances from the fiber/matrix interface.

the ITZ porosity in the very close vicinity of the fiber surface (less than 5 μm) will be influenced by the peeling of the fiber and therefore is prone to error.

3.2 Unhydrated Clinker Gradient

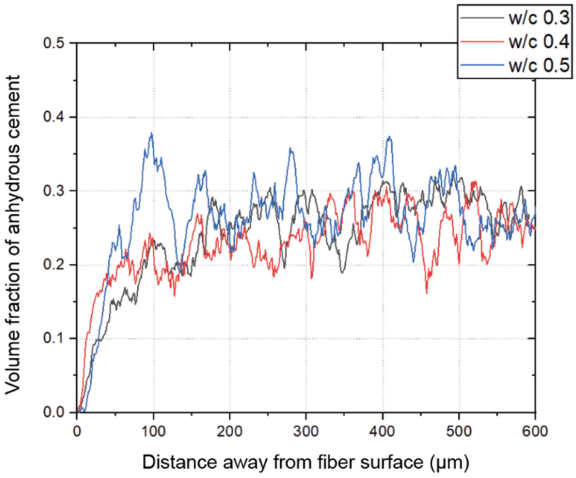

Fig. 6. Volume fraction of anhydrous cement at different distances from the fiber/matrix interface.

By using the same image analysis method, the variation in volume fraction of anhydrous cement adjacent to microfibers can also be obtained based on the BSE imaging analysis. As can be seen from Fig. 6, volume fraction of anhydrous cement is substantially less within the 0–100 μm than the regions far away from the fiber surface. The fact that the zone in the vicinity of the fiber contains significantly less unhydrated cement suggests that there were less cement particles and more water close to the fiber. The particles there thus hydrated faster and easier, resulting in less unhydrated cement. This demonstrates that the packing of the cement grains has indeed been perturbed and becomes rather loose in the region between the fiber and the bulk matrix. This inefficient packing of cement grains may have directly contributed to the high porosity as shown in Fig. 4. These features, including a deficit in anhydrous cement grain and a corresponding high porosity, closely resembles the ITZ between aggregate and cement matrix, indicating that although the diameter of microfibers is small, the axial dimension of microfibers is large enough to act effectively as a 'wall' to perturb the packing of the cement grains surrounding it, resulting in the formation of the ITZ between microfiber and cement matrix.

4 Conclusions

A new approach was proposed to quantitatively characterize the ITZ between microfiber and cement matrix and to reveal its porous microstructure. With the new method, the

porosity of the ITZ between PVA microfiber and cement pastes with different w/c ratios was characterized. Results show that a porous transition zone between micro-fiber and cement matrix exists; and the average thickness of this porous zone is roughly 100 μm. It is also found that the microstructure of ITZ is highly heterogenous along its length direction. At an age of 14 days, the porosity of the ITZ is insensitive to the w/c ratio. It is thus believed that the current method could aid the investigation of fiber/matrix bond performance and also contribute to the development of SHCCs with superior properties.

Acknowledgement.  This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 860006.

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