Quantitative characterization of anisotropic properties of the interfacial transition zone (ITZ) between microfiber and cement paste

He, Shan; Yang, En-Hua; Li, Zhong

2019

He, S., Li, Z., & Yang, E.-H. (2019). Quantitative characterization of anisotropic properties of the interfacial transition zone (ITZ) between microfiber and cement paste. *Cement and Concrete Research*, 122136-146. doi:10.1016/j.cemconres.2019.05.007

<https://hdl.handle.net/10356/105823>

<https://doi.org/214587>;

<https://doi.org/10.1016/j.cemconres.2019.05.007>;

<https://doi.org/214587>

© 2019 Elsevier. All rights reserved. This paper was published in *Cement and Concrete Research* and is made available with permission of Elsevier.

Downloaded on 26 Apr 2023 08:38:13 SGT

Quantitative characterization of anisotropic properties of the interfacial transition zone (ITZ) between microfiber and cement paste

Shan He^a, Zhong Li^b, En-Hua Yang^{a,*}

^aSchool of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

^bSchool of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

Abstract

A new approach to characterize ITZ between microfiber and cement matrix is reported. Results show that microstructure of hydrated cement paste is highly modified in the vicinity of microfibers, with higher porosity and less anhydrous cement. ITZ can extend up to 100 μm from the interface into the matrix. The larger extent of ITZ suggests that perturbation due to inclusion of microfibers to packing of cement grains is severer than that due to inclusion of aggregates. Furthermore, ITZ between microfiber and cement matrix is highly heterogeneous along its axial direction. Existing ITZ analysis methods performed on 2-D cross-sectional plane intersecting with fiber axis thus can lead to errors and uncertainties. Mechanical properties of ITZ between microfiber and cement matrix are anisotropic. Stiffness and ductility of ITZ in the radial direction are 31% and 28% higher than that in the tangential direction, respectively.

Keywords: Interfacial transition zone (B); microstructure (B); fiber reinforcement (E); characterization (B); nanoindentation

* Corresponding author. Address: N1-01b-56, 50 Nanyang Avenue, Singapore 639798. Tel.: +65 6790 5291; fax: +65 6791 0676. E-mail address: ehyang@ntu.edu.sg (E.H. Yang)

1. Introduction

It is well accepted and documented that in cement-based composites, the matrix in the vicinity of an inclusion (*e.g.*, aggregate) can be quite different in its microstructure than the bulk cement matrix. The preferred term used to address this zone is the interfacial transition zone (ITZ) [1-3]. Formation of the ITZ is usually attributed to the ‘wall’ effect [4] which describes the inability of cement grains to pack around the inclusion as densely as they do in the bulk matrix, resulting in higher water-to-cement ratio around the inclusion. Thus, the ITZ is more porous and weaker compared to the bulk matrix, and in many cases governs the mechanical properties and durability of cement-based materials. The influence of ITZ may be amplified when microfibers are included in the cement matrix because microfibers have high aspect ratio, and thus much larger surface area. The ITZ between microfiber and cement-based matrix largely determines the pullout behavior of the fiber from the surrounding matrix [5], which in turn controls the composite performance [6]. For fibers with hydrophilic surface, the bond failure is governed by cohesive fracture in the transition zone [7]. The interfacial bond strength, therefore, is directly influenced by the strength of the transition zone [5]. For fibers with hydrophobic surface, in which adhesive bond failure occurs at fiber/matrix interface, a strong ITZ would also results in higher frictional pullout resistance by sustaining higher circumferential compressive normal stresses that developed as a result of matrix shrinkage [5, 8]. Control of fiber/matrix interfacial properties through tailoring ITZ thus is the key to enhance the performance of microfiber-reinforced cementitious composites [9].

Characterization of the ITZ between aggregate and cement paste have been well studied through scanning electron microscopy (SEM) examination [10-12] and micro-/nano-hardness test [13, 14]. The extent, composition and mechanical properties of the ITZ between aggregate and cement paste have been reported [1-3]. However, there is only few studies reporting the

ITZ between microfiber and cement-based matrix and the results of these studies are sometimes contradictory. Based on SEM observation, 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 [15]. 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 [5] 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. [8] reported that porous ITZ could still be observed even when the w/c of the matrix is as low as 0.2. The presence of a weak ITZ surrounding a microfiber has also been testified by nano-indentation. Nemecek et al. [16] first discovered that mechanical properties of fiber/matrix interface increase with increasing distance from the fiber. Sakulich and Li [17] reported that the elastic modulus of the region within 30 μm from a polyvinyl alcohol (PVA) fiber is noticeably lower than the bulk matrix far from the fiber.

Disagreement among published literatures on the subject matter may be due to the following reasons. Firstly, despite the diameter of microfiber is often small, in the same order of magnitude as that of cement particles, the length of microfiber can be several hundred times of its diameter and is much larger than cement grains. Therefore, microfibers with long fiber length can potentially induce the wall effect of loose packing around the fiber from a 3-dimensional (3-D) space perspective. Furthermore, disturbance of cement packing due to the inclusion of fibers in a 3-D space can be complicated which leads to variation of ITZ properties due to varying packing density along the fiber length as shown in Fig. 1. Secondly, established methods for studying the ITZ often perform analyses on the 2-D cross-sectional plane that

intersect with fiber axis (Fig. 1). Theoretically, to obtain qualitative information from a 3-D heterogeneous structure, the structure of interest has to be sectioned such that resulting sections are both representative of the entire structure and sufficiently large [18, 19]. In the case of the ITZ surrounding aggregates, sections that are made randomly are representative because aggregates have isotropic shape and thus the sectioning is not orientation sensitive; and due to the relatively large particle size of aggregates, the area of the ITZ exposed in these sections is also sufficiently large. Microfibers, however, are highly anisotropic with its length being two to three orders of magnitude larger than its diameter. As illustrated in Fig. 1, the microstructure of the ITZ of 2 sections could be quite different from each other due to the variability along its longitudinal direction. In addition, the area of the annulus ITZ exposed in the 2-D cross-sectional plane perpendicular to fiber axis is also limited due to the small diameter of microfibers.

It is known that circumferential compressive normal stresses due to matrix shrinkage give rise to the frictional pullout resistance of fiber (Fig. 2a). Thus, mechanical properties of ITZ in radial direction (*i.e.*, xx direction) are mostly relevant to the circumferential compressive normal stresses (Figs. 2b and 2c). However, existing methods, such as nano-indentation [20], are often applied to assess mechanical properties of the ITZ in the axial direction (*i.e.*, yy direction). This is again because established methods for studying the ITZ often perform analyses on the 2-D cross-sectional plane that intersect with fiber axis (Fig. 1). Therefore, quantifying mechanical properties of ITZ in radial direction is of great importance and interest for microfiber-reinforced cementitious composites.

To address the research gaps mentioned above, this paper reports a new approach to quantitatively characterize the ITZ between microfiber and cement matrix. Instead of probing

the properties in a small annular ITZ from the axial (yy) direction on the cross-sectional plane perpendicular to the fiber axis, we exposed the ITZ along the longitudinal direction of the fiber axis as shown in Fig. 3 and the properties of ITZ were characterized from the tangential (zz) direction on the large ITZ plane parallel to the fiber axis and from the radial (xx) direction on the interior surface of the fiber groove. In the following sections, methods for sample preparation is presented first, followed by ITZ characterization by means of secondary electron (SE) imaging, backscattered electron (BSE) imaging and nano-indentation.

2. Material and methods

2.1 Material

In this study, CEM I 52.5 N Portland cement was used to prepare a cement paste with a w/c of 0.2 as the matrix. The microfiber used to produce the ITZ is a polyethylene (PE) microfiber (Spectra® 1000, Honeywell) with a diameter of 23 μm . Table 1 summarizes the physical properties and geometry of PE fibers used in this study.

2.2 Sample preparation

To obtain sufficiently large ITZ area for examination, longitudinal section passing through the central axis of the fiber is prepared for ITZ characterization (Fig. 3). As can be seen, long rectangular cross-sections of ITZ and the empty fiber groove (*i.e.*, the interior surface of the hollow cylindrical ITZ) are exposed. This configuration allows the study of the ITZ from two mutually perpendicular directions, *i.e.*, tangential (zz) direction and radial (xx) direction, by performing test on the rectangular cross-sections of ITZ and on the fiber groove, respectively.

Three types of specimens were prepared for ITZ characterization as schematically illustrated in Fig. 4. Specimens with fractured section (Fig. 4a) are prepared for microstructural study of

the ITZ under SE imaging, by which the distribution of microstructural defects along the ITZ can be visualized. Specimens with polished section (Fig. 4b) are prepared for BSE imaging to determine the gradient of anhydrous cement in the ITZ and for nano-indentation to evaluate mechanical properties of the ITZ in the tangential (zz) direction. Specimens with shallow groove (Fig. 4c) are prepared for nano-indentation on the fiber groove to reveal mechanical properties of the ITZ in the radial (xx) direction. Detailed specimen preparation methods can be found in the Appendix.

2.3 Characterization techniques

2.3.1 Microscopy

Optical microscope (OLYMPUS BX51) images and SE images were used to qualitatively study the microstructure of the ITZ. The SE images were acquired by the secondary electron detector in a field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) operating at low voltages (5 keV) to reduce beam/sample interaction volume and at low working distances (3-5 mm) to improve resolution. BSE images of polished sections are used to study the distribution of anhydrous cement in the ITZ. The BSE images were acquired by the BSE detector in the FESEM operating at an accelerating voltage of 15 keV. Surface roughness of polished section was measured by an atomic force microscope (AFM, Park XE-100) at non-contact mode using a silicon nitride cantilever with a spring constant of 40 N/m and a resonance frequency of 300 kHz.

2.3.2 BSE image analysis

BSE image analysis has been well established as a quantitative method for the study of concrete microstructure [2, 10-12]. In BSE images, contrast in grey level is produced primarily by mean atomic number variations of different phases, which enables both the discrimination of

individual microstructural components and the assessment of their spatial distribution. Fig. 5a shows a typical BSE image of specimen with polished surface, which was made by electronically ‘stitching’ eight BSE images taken at a nominal magnification of $\times 500$. Contrast in the BSE image yields clear definition of constituents, *e.g.*, the region in light gray corresponds to the anhydrous cement. Fig. 5b shows the binary image with black pixels representing the anhydrous cement after post-image processing. The area fraction of anhydrous cement in each band ($10 \times 1000 \mu\text{m}^2$) was determined by calculating the percentage of black pixels over all pixels in the band. A total of 5 specimens with identical groove length of 1 mm were examined. The mean value and corresponding standard deviation were reported.

2.3.3 Nano-indentation

Mechanical properties of the ITZ were investigated by means of an Agilent G200 Nano Indenter fitted with a Berkovich tip. Indentation tests were carried out by depth-sensing techniques with the continuous stiffness measurements (CSM) option, which allows the hardness and elastic modulus to be recorded as a function of contact depth in a single indentation. A detailed description of the CSM depth-sensing tests and analysis method can be found in [21].

Nano-indentations were carried out on the large rectangular cross-sections of ITZ in specimens with polished section to evaluate mechanical properties of the ITZ in the tangential (zz) direction (Fig. 4b). The indentation depth for each test was set to be 500 nm. The mean hardness and the mean modulus of each indent were determined from the CSM indentation curve by averaging the hardness (or modulus) value between 100 nm and 500 nm indentation depth. For each specimen, several lines of indents were produced parallel to the edge of the fiber groove with a spacing of $10 \mu\text{m}$ as shown in Fig. 6. After the nano-indentation tests, all specimens

were investigated by both SE image and BSE image analyses. From BSE images, the corresponding phase where each indent was produced was subsequently revealed. The indents on anhydrous cement grains were deliberately excluded for only the properties of the hydration product in the ITZ is of interest to this study. From SE images, the distance of the indents to the fiber groove could be determined. The indents were categorized into 4 groups according to their respective distance, *i.e.*, 0-10 μm , 10-20 μm , 20-30 μm , and 30-40 μm , from the fiber/matrix interface. For each group, at least 50 indents were included and statistically evaluated.

Nano-indentations were carried out on the empty fiber groove in specimens with shallow groove to evaluate mechanical properties of the ITZ in the radial (xx) direction (Fig. 4c). The tests were carried out to a maximum indentation depth of 1000 nm. The mean hardness and the mean modulus of each test were determined from the CSM indentation curve by averaging the hardness (or modulus) value between 200 nm and 1000 nm indentation depth. The spacing is set to be 20 μm . At least 60 indents were included and statistically evaluated.

3. Results and discussion

3.1 Microstructure of the ITZ

Fig. 7a shows a typical stitched SE image of the ITZ between PE microfiber and cement matrix in the specimen with fractured section (Fig. 4a). A fiber groove can be easily identified at the center of the graph. High porosity in the size of several tens of micron could be seen at the groove and in its vicinity. On the contrary, the matrix far away from the groove is very dense without noticeable defects. This drastic contrast in microstructure between the bulk and the area near the fiber groove suggests existence of a porous transition zone between microfiber and cement matrix. Fig. 7b shows a stitched BSE image of ITZ in the specimen with polished

section, in which anhydrous cement and hydrated phase can be distinguished on the basis of their grey level in the image. The fiber groove appeared as a shadowy rectangle at the center of the image as a result of its concave topography. As can be seen, the zone in the vicinity of the fiber groove contains predominately small grains, while larger grains are further out, suggesting that the packing of the cement grains has been perturbed and becomes rather loose in the region between the fiber groove and the bulk matrix. This inefficient packing of cement grains may have directly contributed to the high porosity that is observed in the SE image. 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. It should be noted that the w/c adopted in this study is 0.2, which is nearly the lowest that could be adopted in fiber-reinforced cementitious composites. Thus, the results of current study indicate the widespread presence of the ITZ in microfiber-reinforced cementitious composites with varied mixture composition.

Furthermore, from the SE image, it can be found that porosity in the ITZ is not homogeneous along the fiber groove. Concentration of pores can be seen at some locations, while some areas remain intact. From the BSE image, this variability is more obvious as the width of the band with noticeably less anhydrous cement grains changes considerably along both sides of the fiber groove, as indicated by the white dash lines in Fig. 7b. This reveals that the ITZ between microfiber and cement paste is highly heterogenous along its axial direction. As a result, existing ITZ analysis methods performed on the 2-D cross-sectional plane intersecting with fiber axis can lead to errors and uncertainties.

3.2 Anhydrous cement in the ITZ

Fig. 8 shows the variation in volume fraction of anhydrous cement adjacent to microfibers based on the BSE imaging analysis. As can be seen, volume fraction of anhydrous cement increases with increasing distance from fiber/matrix interface. The increment rate is high within 0-40 μm from the interface, rising to about 20%. Moderate increment is observed beyond 40 μm , reaching to around 26% at 100 μm from the interface, which could be considered as the bulk matrix. It has been reported that the volume fraction of anhydrous cement for a cement paste with same w/c of 0.2 is around 30% [22], which is in good agreement of the current results.

The results suggest that the microstructure of the hydrated cement paste is highly modified in the vicinity of microfibers, extending up to 100 μm from the interface into the matrix with the most significant deficit in anhydrous cement being in the region of about 40 μm adjacent to the fiber. The zone with a reduced amount of anhydrous cement surrounding a fiber is even wider than that around aggregates, which has been published as in a range of 50 μm [1]. This may be due to that aggregates have curved and uneven surfaces, which facilitate the packing of cement grains to some extent. The long microfiber, however, is perfectly flat and thus may have acted more effectively as a 'wall', resulting in a poor packing in the vicinity of interface and a wider apparent width of the ITZ. In fact, it has been reported that the geometric interactions between particles and fibers are also strongly affected by the aspect ratio and the rigidity of the fiber [23, 24], indicating the perturbation created by the fibers may be more complicated than that created by aggregates.

Given the relatively large zone in which the packing of the cement grains is disrupted by the fiber, it is expected the total volume of the ITZ may comprise a high proportion of the

composite. For microfiber-reinforced cementitious composites, the volume fraction of the fiber used could be around 2%. Even if the width of the ITZ is considered as only 40 μm , which is the region with the most significant changes in the amount of anhydrous cement, the volume of the hollow cylindrical ITZ would be 24 times of the volume of the fiber as the outer diameter of the ITZ is 5 times that of a fiber. If no overlap between the ITZs is assumed, the overall volume of the ITZ may take up around 50% of the composite. As the ITZ is more porous than the bulk matrix, the properties of the ITZ could have significant impacts on the mechanical and transport properties of the composite materials.

3.3 Anisotropic properties of the ITZ

Fig. 9 presents typical CSM nano-indentation curves measured from the tangential (zz) and the radial (xx) directions. As can be seen, indentation modulus measured from the tangential (zz) direction remains steady after an initial fluctuation which could be attributed to the surface texture of the fiber groove. However, indentation modulus measured from the radial (xx) direction increases with increasing indentation depth. This suggests the ITZ between microfibers and cement matrix in the current study may have a concentric laminated microstructure. This may be due to the ‘one-sided’ growth of hydrates [25]. In the bulk paste, pore space may become filled with hydrates by the migration of species from all directions. Close to the interface, however, hydrates migrate only from the cement paste side. As a result, the amount of the hydration products precipitated at different distance from the fiber surface to the nearest cement particle would vary, leading to a layered microstructure.

Fig. 10 plots the mean modulus and the mean hardness measured from the tangential (zz) direction as a function of distance from fiber/matrix interface. The mean modulus and the mean hardness measured from the radial (xx) direction are also included in the figure. The box in the

chart indicates the range from one standard deviation below the mean (-SD) to one standard deviation above the mean (+SD) and the whiskers showing the extremes. Specific values for the respective groups are also summarized in Table 2. As can be seen, both the mean elastic modulus and the mean hardness increase with increasing distance from fiber/matrix interface. The mean elastic modulus in the 0-10 μm region is only 77% that of the 20-40 μm region from the interface.

It should be noted that the standard deviations of both the mean modulus and the mean hardness in the 0-10 μm region are the largest compared to other regions, demonstrating again the microstructure developed near the fiber is highly heterogeneous. The implication of this could be significant because during fiber debonding or pullout, microcracks would preferably initiate from the weakest regions in the ITZ. Thus, it is plausible that this weak and highly heterogeneous 10- μm -wide region near the interface is the most critical zone that governs the load transfer and composite performance. This may also suggest that strengthening of the ITZ should target for this region.

The mean modulus and the mean hardness measured from the radial (xx) direction are 37.09 ± 10.20 GPa and 1.48 ± 0.53 GPa, respectively, as shown in Figs. 10a and 10b (the leftmost boxes). As the properties in the radial (xx) direction are more relevant to the circumferential compressive normal stresses that give rise to the frictional pullout resistance of fiber, they should be used to describe the ability of the ITZ to resist decay or failure during the process of fiber pullout. Furthermore, the average radial (xx) modulus (37.09 ± 10.20 GPa) is 31% higher than the average tangential (zz) modulus near the interface (0-10 μm : 28.23 ± 13.03 GPa). This suggests mechanical properties in the ITZ are anisotropic.

It should be noted that the degree of anisotropy measured in the current study is an average property of the volume of material sensed by indenter during indentation. As the ITZ has a concentric graded microstructure, its properties are expected to change continuously in its radial direction, and thus the degree of anisotropy within the unit volume may not necessarily be a constant value, but most likely to be a function of the distance from the interface. However, estimation of the plasticity or elasticity gradient of compositionally graded materials through indentation is much more complicated and requires priori-knowledge of the graded material such as its average Poisson ratio and experimentally-determined load-displacement curves of indentation performed at homogeneous materials which comprise the phases of the graded layers [26-29], which are all currently unavailable. More comprehensive studies on the property gradient of the ITZ are needed to obtain a more quantitative understating to determine the best resolution for the quantification of the anisotropy of the ITZ.

To further investigate this anisotropic response, the mean modulus is plotted against the mean hardness of each indent measured from the tangential (zz) direction (0-10 μm) as well as from the radial (xx) direction (Fig. 11). As can be seen, with a given mean hardness, the mean radial (xx) modulus is higher than the mean tangential (zz) modulus, *i.e.*, the ITZ is stiffer in the radial direction than the tangential direction. The mean modulus-to-hardness (M/H) ratio (*i.e.*, slope of the fitted curve in Fig. 11) can be used to assess ductility of material [30, 31] because it represents the spatial extent of the elastic deformation that might occur under loading before permanent yielding occurs in the indentation test [32]. As can be seen, the mean radial (xx) M/H ratio (24) is 28% higher than the mean tangential (zz) M/H ratio (18.8), suggesting that the yield strain of the ITZ is anisotropic as well and the ITZ from the radial direction is more ductile than that from the tangential direction. It should be noted that the influence of ductility of the ITZ on the properties of composite is not straightforward. A more ductile ITZ may not

necessarily lead to improved composite ductility because ductility of fiber-reinforced cementitious composites is determined by the number of cracks formed as well as opening of each crack. A ductile ITZ, however, may affect the stress vs crack opening relation, which can be viewed as the constitutive law of fiber-bridging behavior. In the state-of-the-art micromechanics-based fiber-bridging model, the energetics of tunnel crack propagation along fiber/matrix is used to quantify the debonding process and the bridging force of a fiber with given embedment length [33]. A more ductile ITZ could result in higher fracture energy of the fiber/matrix interface which could lead to higher energy-dissipation during the fiber pullout and potentially higher fiber pullout force. Future research is necessary to have a better understanding of this point.

The anisotropic response of the ITZ seems to be a reasonable consequence of having a concentric laminated microstructure as indicated by the CSM curve (Fig. 9). Furthermore, the precipitation of calcium hydroxide in the ITZ may have also contributed to this anisotropic effect. It has been reported that there is a preferential orientation of calcium hydroxide with the c-axis parallel to the aggregate surface [34]. Further study is necessary to reveal the exact origins of the anisotropic properties of the ITZ.

The anisotropic behavior of the ITZ between microfiber and cement matrix is significant. Firstly, understanding this behavior may facilitate the study of the failure mechanisms of the interfacial bond between fiber and cement matrix. Secondly, it is also expected to enhance the predictability of existing analytical and numerical models for fiber-reinforced concrete, in which the ITZ is treated as isotropic. Lastly, it should be noted this anisotropic response should not be exclusive to the ITZ surrounding microfibers. The ITZ between aggregate and cement

paste may also be anisotropic. Future studies are needed to address the effects of anisotropy on the overall performance of concrete.

4. Conclusions

A new approach was proposed to quantitatively characterize the ITZ between microfiber and cement matrix and to reveal its anisotropic properties. In this study, the ITZ between PE microfiber and cement paste was characterized from the tangential (zz) direction on the large ITZ plane parallel to the fiber axis and from the radial (xx) direction on the interior surface of the fiber groove. A sample preparation method revealing the ITZ along the longitudinal direction of the fiber with high quality surface finishing was developed. The microstructure, gradient of anhydrous cement, and mechanical properties of the ITZ were studied by means of SE imaging, BSE imaging and nano-indentation.

Results show that microstructure of the hydrated cement paste is highly modified in the vicinity of microfibers, with higher porosity and less anhydrous cement. The ITZ can extend up to 100 μm from the interface into the matrix with the most significant deficit in anhydrous cement in the region of about 40 μm adjacent to the fiber. The larger extent of the ITZ suggests that perturbation due to the inclusion of microfibers to the packing of cement grains is severer than that due to the inclusion of aggregates. Furthermore, the ITZ between microfiber and cement matrix is highly heterogeneous along its axial direction. Thus, existing ITZ analysis methods performed on the 2-D cross-sectional plane intersecting with fiber axis can lead to errors and uncertainties. Mechanical properties of ITZ between microfiber and cement matrix are anisotropic. Stiffness and ductility of the ITZ in the radial (xx) direction are 31% and 28% higher than that in the tangential (zz) direction, respectively. Further study is necessary to

reveal the exact origins of the anisotropic properties of the ITZ and to address potential effects of ITZ anisotropy on the overall performance of cement-based composites.

Acknowledgements

The authors would like to thank the funding support for this project from Land and Livability National Innovation Challenge, Ministry of National Development, Singapore (L2NICCFP2-2015-4).

References

- [1] J. Ollivier, J. Maso, B. Bourdette, Interfacial transition zone in concrete, *Advanced Cement Based Materials*, 2 (1995) 30-38.
- [2] K.L. Scrivener, A.K. Crumbie, P. Laugesen, The interfacial transition zone (ITZ) between cement paste and aggregate in concrete, *Interface science*, 12 (2004) 411-421.
- [3] M. Alexander, Engineering and transport properties of the interfacial transition zone in cementitious composites, *Rilem Publications* 1999.
- [4] D. Pinchin, D. Tabor, Interfacial phenomena in steel fibre reinforced cement I: Structure and strength of interfacial region, *Cement and concrete research*, 8 (1978) 15-24.
- [5] Y.W. Chan, V.C. Li, Effects of transition zone densification on fiber/cement paste bond strength improvement, *Advanced cement based materials*, 5 (1997) 8-17.
- [6] V.C. Li, H. Stang, Interface property characterization and strengthening mechanisms in fiber reinforced cement based composites, *Advanced cement based materials*, 6 (1997) 1-20.
- [7] T. Kanda, V.C. Li, Interface property and apparent strength of high-strength hydrophilic fiber in cement matrix, *Journal of materials in civil engineering*, 10 (1998) 5-13.
- [8] S. He, J. Qiu, J. Li, E.H. Yang, Strain hardening ultra-high performance concrete (SHUHPC) incorporating CNF-coated polyethylene fibers, *Cement and Concrete Research*, 98 (2017) 50-60.

398 [9] V.C. Li, H. Wu, Y. Chan, Interface property tailoring for pseudo strain-hardening
399 cementitious composites, *Advanced Technology for Design and Fabrication of Composite*
400 *Materials and Structures*, Springer1995, pp. 261-268.

401 [10] K.L. Scrivener, H. Patel, P. Pratt, L. Parrott, Analysis of phases in cement paste using
402 backscattered electron images, methanol adsorption and thermogravimetric analysis, *MRS*
403 *Online Proceedings Library Archive*, 85 (1986).

404 [11] K.L. Scrivener, Backscattered electron imaging of cementitious microstructures:
405 understanding and quantification, *Cement and Concrete Composites*, 26 (2004) 935-945.

406 [12] K. Scrivener, R. Snellings, B. Lothenbach, *A practical guide to microstructural analysis*
407 *of cementitious materials*, Crc Press2016.

408 [13] T.Y. Lyubimova, E. Pinus, Crystallization structure in the contact zone between aggregate
409 and cement in concrete, *Colloid J. USSR*, 24 (1962) 491-498.

410 [14] S. Zhao, W. Sun, Nano-mechanical behavior of a green ultra-high performance concrete,
411 *Construction and Building Materials*, 63 (2014) 150-160.

412 [15] A. Katz, A. Bentur, Mechanical properties and pore structure of carbon fiber reinforced
413 cementitious composites, *Cement and concrete research*, 24 (1994) 214-220.

414 [16] J. Nemecek, P. Kabele, Z. Bittnar, Nanoindentation based assessment of micromechanical
415 properties of fiber reinforced cementitious composite, *6th International RILEM Symposium*
416 *on Fibre Reinforced Concretes*, RILEM Publications SARL, 2004, pp. 401-410.

417 [17] A.R. Sakulich, V.C. Li, Nanoscale characterization of engineered cementitious composites
418 (ECC), *Cement and Concrete Research*, 41 (2011) 169-175.

419 [18] H. Elias, D.M. Hyde, An elementary introduction to stereology (quantitative microscopy),
420 *Am J Anat*, 159 (1980) 412-446.

421 [19] Crumbie, A. Kim, *Characterisation of the microstructure of concrete*, Imperial College
422 *London (University of London)*, 1994.

423 [20] L. Sorelli, G. Constantinides, F.J. Ulm, F. Toutlemonde, The nano-mechanical signature
 424 of ultra high performance concrete by statistical nanoindentation techniques, *Cement and*
 425 *Concrete Research*, 38 (2008) 1447-1456.

426 [21] X. Li, B. Bhushan, A review of nanoindentation continuous stiffness measurement
 427 technique and its applications, *Materials characterization*, 48 (2002) 11-36.

428 [22] M. Vandamme, F.J. Ulm, P. Fonollosa, Nanogranular packing of C-S-H at
 429 substoichiometric conditions, *Cement and Concrete Research*, 40 (2010) 14-26.

430 [23] F. De Larrard, *Concrete mixture proportioning: a scientific approach*, CRC Press 2014.

431 [24] N. Roussel, *Understanding the rheology of concrete*, Elsevier 2011.

432 [25] E.J. Garboczi, D.P. Bentz, Digital simulation of the aggregate-cement paste interfacial
 433 zone in concrete, *Journal of materials Research*, 6 (1991) 196-201.

434 [26] I. Choi, M. Dao, S. Suresh, Mechanics of indentation of plastically graded materials-I:
 435 Analysis, *Journal of the Mechanics and Physics of Solids*, 56 (2008) 157-171.

436 [27] I. Choi, A. Detor, R. Schwaiger, M. Dao, C. Schuh, S. Suresh, Mechanics of indentation
 437 of plastically graded materials-II: Experiments on nanocrystalline alloys with grain size
 438 gradients, *Journal of the Mechanics and Physics of Solids*, 56 (2008) 172-183.

439 [28] A. Giannakopoulos, S. Suresh, Indentation of solids with gradients in elastic properties:
 440 Part II. Axisymmetric indentors, *International Journal of Solids and Structures*, 34 (1997) 2393-
 441 2428.

442 [29] A. Giannakopoulos, S. Suresh, Indentation of solids with gradients in elastic properties:
 443 Part I. Point force, *International Journal of Solids and Structures*, 34 (1997) 2357-2392.

444 [30] C.G. Hoover, F.J. Ulm, Experimental chemo-mechanics of early-age fracture properties
 445 of cement paste, *Cement and Concrete Research*, 75 (2015) 42-52.

- 446 [31] M.A. Qomi, K. Krakowiak, M. Bauchy, K. Stewart, R. Shahsavari, D. Jagannathan, D.B.
447 Brommer, A. Baronnet, M.J. Buehler, S. Yip, Combinatorial molecular optimization of cement
448 hydrates, *Nature communications*, 5 (2014) 4960.
- 449 [32] A.C. Fischer-Cripps, *Nanoindentation*, Springer New York 2013.
- 450 [33] E.H. Yang, S. Wang, Y. Yang, V.C. Li, Fiber-bridging constitutive law of engineered
451 cementitious composites, *Journal of advanced concrete technology*, 6 (2008) 181-193.
- 452 [34] J. Larbi, J. Bijen, Orientation of calcium hydroxide at the Portland cement paste-aggregate
453 interface in mortars in the presence of silica fume: A contribution, *Cement and Concrete*
454 *Research*, 20 (1990) 461-470.
- 455 [35] M. Miller, C. Bobko, M. Vandamme, F.J. Ulm, Surface roughness criteria for cement paste
456 nanoindentation, *Cement and Concrete Research*, 38 (2008) 467-476.
- 457

Appendix – Detailed Sample Preparation Method

To prepare the specimen, a long PE fiber was cut into about 150 mm in length and fixed at the center of a prismatic mold. The fresh cement paste was prepared and cast into the mold (Fig. A.1a, top). The molds were covered with plastic sheets and cured in air at room temperature for one day. The hardened specimens were then removed from the molds and cured in lime-saturated water for another 27 days in the laboratory at a temperature of $23 \pm 3^{\circ}\text{C}$ before further processing.

The cement paste prism embedded with one continuous fiber was then sliced into thin plate-like specimens of 1 mm thick with the help of a diamond saw and isopropyl alcohol as a cutting lubricant (Fig. A.1a, middle). Each resulting specimen would have a segment of fiber embedded in its center position perpendicular to its front surface (Fig. A.1a, bottom). Specimens with fractured section were prepared by creating a sharp surface notch on the front surface passing through the fiber using a utility knife and extending a crack through the notch to cleave the specimen. For the other two types of specimens, the thin plate-like specimen was trimmed down from the top to the dashed line in Fig. A.1a (bottom), which is roughly 1 mm above the fiber. The trimmed specimen was then glued to a plastic cubic holder (Fig. A.1b) which allows two orientations, one for grinding (Fig. A.2a) and the other for monitoring (Fig. A.2b). In the standing orientation (Fig. A.2a, top), the specimen surface to be grinded is facing upward, allowing the removal of material from the uppermost. Fig. A.2a (bottom) shows SEM micrographs of a specimen before and after some grinding in the standing position. In the lying orientation (Fig. A.2b, top), the specimen could be examined under an optical microscope in transmitted light mode to monitor the progress of grinding. Since the polymeric fiber is transparent in nature, the position of the fiber could be easily distinguished as a bright dot as

shown in Fig A.2b (bottom). This allows timely monitoring of the grinding to reach the required depths for BSE imaging and nano-indentation tests (Fig. 4). In this study, for specimens with polished section, the grinding was stopped at exactly the center of the fiber, producing a fiber groove with a depth equivalent to the radius of fiber. For the specimens with shallow groove, the grinding was controlled with great care to craft a shallow groove to allow the indenter reaching the bottom of the groove. Given that the equivalent cone angle of a berkovich indenter is 70.32° and the diameter of the fiber groove is $23\text{ }\mu\text{m}$, it can be calculated that around 82% of the depth of the groove have to be grinded away to avoid the edge of the groove colliding with the indenter before the bottom of the groove (Fig. A.3a). Fig. A.3b shows a SEM micrograph of a specimen after the groove depth reduction.

An in-house designed grinding and polishing system, which consists of a rotary machine on the top facing downwards and a precise z-axis stage (accuracy: $10\text{ }\mu\text{m}$) on the bottom as shown in Fig. A.4, was developed for the controlled grinding. The rotary machine and the z-axis stage are fixed firmly onto a frame to minimize the vibration during operation. The rotary machine is used to drive a lapping wheel attached with abrasive media and operates at speeds up to 35,000 revolutions per minutes. The specimen (on holder) was glued to an alumina plate fixed on the z-axis stage by screws (Fig. A.4a). By increasing the height of the z-axis stage and forcing the top surface of the specimen to contact the rotating wheel, the abrasive could therefore travel across the sample surface and grind the surface by pushing, rolling, and scratching behaviors of the abrasives. It is critical to increase the height of the z-axis stage slowly so that normal force applied to the specimen during grinding, the main cause of stress concentration between the fiber and matrix interface which leads to the erosion of the ITZ and unevenness of the finished surface, can be minimized. In this study, P1200 grit abrasive paper is used for flattening the fracture surface, and P2500 grit abrasive paper is used for slowly

reaching desired section. The grinding was operated in an intermittent way, with each round include 3 seconds of grinding and monitoring of the grinding process. After grinding, the specimen is cleaned in isopropyl alcohol in an ultrasonic bath for 1 min.

To further improve the quality of the surface finishing, the specimen is polished by using the same set-up in the same manner but with a polishing wheel (Fig. A.4b). The wheel was mounted with a synthetic silk polishing cloth (VerduTex from Buehler) charged with 1 μm diamond paste. The relatively soft cloth is to ensure the fine abrasives are elastically sustained in the cloth, thus creating the least amount of large chips during polishing. The advantage of using only one size of diamond has been described in [35]. Ethanol and 1,4 butanediol (1:1) was also charged onto the cloth to dissipate any heat built-up. Similarly, increase of the height of the z-axis stage should be slow during polishing as well. 3 to 5 seconds of polishing time is sufficient to yield a smooth surface. Extended duration has negative effects because the debris removed from the specimen surface could easily accumulated on the polishing cloth, resulting in deep scratches on the specimen. After polishing, the specimen is then cleaned in an ultrasonic bath again for 1 min.

Figs. A.5a and A.5b show the typical optical microscope images of a specimen after grinding and polishing, respectively, in which a fiber groove at the center of the specimen was exposed. As can be seen, the groove is preserved and the ITZ along the groove is visually as smooth as the bulk matrix away from the groove. Fig. A.5c shows a SEM micrograph of the same specimen after polishing, in which a region near the end of the groove was scanned by AFM. Fig. A.5d shows the AFM image of this 40 μm by 40 μm region, it can be seen that the scanned area except for the groove is extremely flat. The calculated average root-mean-squared (RMS) roughness of the flat region in this figure and several regions randomly selected around the

groove is 59.47 nm, which satisfies the criteria for nano-indentation as proposed in published literature [35]. The sample preparation method developed in this study reveals large ITZ region with high quality finishing which enables the study of the ITZ from tangential (zz) direction and radial direction by performing test on the rectangular cross-sections of ITZ and fiber groove, respectively (Fig. 4).

540 **Tables**

541

542 Table 1. Properties of the PE fibers (Spectra® 1000, Honeywell)

Diameter (μm)	Length (mm)	Tensile strength (MPa)	Elastic modulus (GPa)	Density (g/cm^3)
23	19	3250	113	0.96

543

544

545

Table 2. Mechanical properties of the ITZ determined by nano-indentation

Mechanical properties		Measured from radial direction (GPa)	Measured from circumferential direction (GPa)			
			Distance from fiber/matrix interface (μm)			
			10	20	30	40
Indentation Modulus	Mean	37.09	28.23	36.44	36.78	37.60
	COV	27.51%	46.16%	23.98%	19.45%	18.42%
	+SD	47.29	41.26	46.11	45.61	46.54
	-SD	26.88	15.20	26.77	27.96	28.67
Indentation Hardness	Mean	1.48	1.57	1.67	1.78	1.69
	COV	35.94%	41.62%	26.37%	32.53%	25.19%
	+SD	2.01	2.22	2.17	2.25	2.18
	-SD	0.95	0.91	1.17	1.31	1.21

546

547

Figures

Fig. 1. Schematic illustrations of the axial variability of the ITZ surrounding a microfiber.

Fig. 2. Schematic illustration of the 3 directions of the ITZ surrounding a microfiber.

Fig. 3. Schematic illustration of a longitudinal section of the ITZ containing rectangular cross-sections of the ITZ and an empty fiber groove.

Fig. 4. Schematic illustration of 3 types of specimens and respective tests.

(a)

(b)

Fig. 5. (a) BSE image of specimen with polished surface, and (b) binary image converted from the BSE image with the grids indicating the bands.

Fig. 6. SE images of residual indents on a cross-section of the ITZ.

(a)

(b)

Fig. 7. (a) SE image of the ITZ between a PE fiber and cement paste in the specimen with fractured section, and (b) BSE image of ITZ in the specimen with polished section.

Fig. 8. Volume fraction of anhydrous cement at different distances from the fiber/matrix interface.

Fig. 9. Typical CSM nano-indentation curves measured from the tangential (zz) direction and the radial (xx) direction.

(a)

(b)

Fig. 10. (a) Mean modulus and mean hardness of the ITZ measured from the tangential (zz) direction as a function of distance from fiber/matrix interface, and (b) mean modulus and mean hardness measured from the radial (xx) direction.

Fig. 11. Mean modulus and mean hardness of each indent measured from the tangential (zz) direction (0-10 μm) and the radial (xx) direction.

Fig. A.1. (a) Preparation of a mounted specimen, and (b) overview photograph of the mounted specimen.

Fig. A.2. Two orientations of the specimen for (a) grinding/polishing, and (b) monitoring.

598

599

600 Fig. A.3. (a) Schematic illustration of groove depth reduction, and (b) SE image of a fiber
601 groove after depth reduction.

602

Fig. A.4. (a) Schematic illustration of the set-up used for grinding and polishing, (b) photograph of lapping wheels with different abrasive media, and (c) photograph of the manual z-axis stage.

Fig. A.5. Optical microscope images of a specimen (a) after grinding and (b) after polishing, (c) SE image and (d) AFM scanning of a polished section with fiber groove.