Effect of shrinkage reducing admixture on new-to-old concrete interface

Renyuan Qin\textsuperscript{a}, Huali Hao\textsuperscript{a}, Theodoros Rousakis\textsuperscript{b}, Denvid Lau\textsuperscript{a,c,∗}

\textsuperscript{a} Department of Architecture and Civil Engineering, City University of Hong Kong, Hong Kong, China
\textsuperscript{b} Department of Civil Engineering, Democritus University of Thrace (DUTH), Xanthi, Greece
\textsuperscript{c} Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA

\textbf{A B S T R A C T}

New-to-old concrete interfaces can be widely seen in the process of repairing or strengthening concrete structures, such as concrete jacketing and concrete overlay or repair mortar (high performance fiber reinforced one included etc.) or self-consolidated concrete or self-consolidated mortar. One major difference between new and old concrete is that the shrinkage of new concrete is much higher than that of old concrete during its hardening process. This difference in volume change results in the incompatibility between old concrete and new concrete (as strengthening and repair material). Moreover, prior research studies in this area indicate that such incompatibility between new and old concrete can result in the development of stress concentration at the interface, leading to cracks and premature failure of the repair overlay. The cracks provide access for free water carrying chloride ions or carbon dioxide, which further reduces the durability of a new-to-old concrete system. The usage of shrinkage reducing admixture (SRA) in new concrete design can reduce the shrinkage of new concrete by reducing the surface tension of water. Moreover, it is reported that SRA can reduce the water diffusivity in concrete in order to achieve an enhanced durability. To study the effect of SRA on the interfacial integrity of a new-to-old concrete system, an experimental study was first conducted to investigate the interfacial fracture toughness of the new-to-old concrete system. It was found that the interfacial fracture toughness could be increased by adopting SRA in the design mix of new concrete. Moreover, when the samples were exposed to moist conditions, the decreasing rate of interfacial fracture toughness was lower when SRA was adopted in the design mix, which indicates that the new-to-old system is more durable in moist condition with SRA. To explore water transition behavior at the new-to-old concrete interface, molecular dynamics simulations have been performed. Based on the results from molecular dynamics simulations, it is revealed that the use of SRA can reduce the water diffusion coefficient at pores around new-to-old interface, so that a more durable performance can be achieved when the system is under moisture attack. The finding provides insightful information on the role of SRA in the interfacial integrity and durability of the new-to-old concrete system and may cover strengthening jackets and repair mortars.

\textbf{1. Introduction}

New-to-old concrete interfaces appear in existing civil infrastructure whenever there is a need to deal with maintenance and repair, such as old concrete structures strengthened with new reinforced concrete jackets, concrete overlays or repair mortars with mass fiber reinforcement (high performance mortars, etc.), and self-consolidated concretes or mortars [1–5]. The interfacial failure often leads to delamination of repair material and/or spalling resulting in a reduction in the service life of the repaired structure [6,7]. In order to make sure that such repair schemes are lasting, one must pay attention to the material bonding between newly applied concrete and old concrete substrate [8]. Interfacial failure is generally caused by incompatibility due to the difference in shrinkage strain between the old concrete substrate and the newly applied concrete [9–14]. Shrinkage is the volumetric changes of concrete structures due to the loss of moisture by evaporation. The shrinkage of repair material cannot proceed freely due to the restraint provided by the substrate at interface. This results in the development of stress concentration at the interface, leading to a premature failure of repair overlay [15–20]. The potential failure modes include vertical cracking due to direct tension, horizontal cracking due to transverse or peeling tensile stresses, and delamination due to interface shear stresses. The problem becomes even more serious if the repaired structure is subjected to an aggressive environment such as a moist one, with cracks providing access for free water, chloride ions and carbon dioxide. Thus, the compatibility of the concrete substrate and repair
layer should be optimized to improve the effectiveness and durability of repaired concrete structures [8,9,12].

The shrinkage reducing admixture (SRA) is one of the most readily used admixtures in cementitious material for reducing shrinkage, and has been adopted in the repairing overlay to enhance its compatibility with concrete substrate [21,22]. The working principle of SRA is to reduce the water surface tension in capillary pores. Many studies have been conducted to evaluate the performance of SRA adopted in conventional concrete or other cementitious overlays, and it is reported that shrinkage and cracks due to restrained shrinkage can be reduced by such admixture [23–25]. Moreover, it is also reported that SRA can reduce the sorptivity and wetting moisture diffusivity of materials, which can improve the durability of concrete under moist conditions [26,27]. However, previous research is mainly focused on the effect of SRA on repair material itself, and whether such durability improvement can be achieved in new-to-old concrete bonding system is still to be understood. Hence, the effect of SRA on interfacial properties and durability of new-to-old concrete under moist conditions needs to be rigorously addressed. In order to capture the failure process of local debonding regions, fracture-based approach is more favorable than a strength-based approach [28–31]. The fracture-based approach provides an initial step for understanding how a local crack can result in a global structural failure. The interfacial fracture toughness can be measured to quantify the resistance to crack initiation in local regions, and to predict the crack propagation using experimental studies. Moreover, the durability improvement of concrete by SRA should be related to its impact on water structure and dynamics in pore solutions. Due to the material purity and instrument accuracy, investigating the water structure and dynamics in concrete material by experiments alone is challenging. Computational methods can help to interpret the experimental results, which play a complementary role in understanding the structural and dynamic properties of water in the pores of cementitious material at molecular level. To investigate the water transport behavior at interface, a molecular model that displays the interaction between SRA and water in pore structures at new-to-old concrete interface can help to elucidate the mechanism of SRA in reducing the sorptivity and wetting moisture diffusivity at the molecular level.

The objectives of this study are to investigate the effect of SRA on interfacial fracture toughness at the new-to-old concrete interface, and to probe the role of SRA in water diffusivity at the interface of new-to-old concrete in a fundamental manner. Four-point bending tests were carried out to measure the interfacial fracture toughness for specimens conditioning under both dry and moist conditions in order to characterize the interfacial behavior in terms of interfacial fracture toughness and failure mode. Illustrated with molecular dynamics (MD) simulations, the role of SRA and water molecules on affecting the interfacial bonding and water diffusion is explored.

The results of this study provide recommendations for more systematic and durable materials to resist the delamination and spalling failures of repaired concrete structures. The idea is to optimize the compatibility of the existing structure and repair material in order to reduce the interfacial cracks, and to reduce the water diffusion at interface between old concrete substrate and repair material, which helps to enhance the life-time of repaired concrete structures. Moreover, the findings in this research can provide the information on the importance of SRA that can be included in the product development for the repair of concrete structures.

2. Materials and methods

2.1. Material properties and sample preparation

The same concrete design was used in this study for both the old and new concrete without admixture, as shown in Table 1. Two types of old concrete samples were cast two years before and kept in lab condition, i.e. concrete cube (150 mm × 150 mm × 150 mm corresponds to width × height × length) and concrete beam (100 mm × 100 mm × 500 mm corresponds to width × height × length). Three concrete cubes were cast for compressive test to determine the compressive strength and Young's Modulus of concrete. Each old concrete beam sample was cut into two specimens with the dimensions of 100 mm × 100 mm × 250 mm, and the cut surface was used to be bonded with new concrete. Before bonding to the new concrete, the old concrete samples were immersed in water for 24h to achieve full saturation and then dried in air for 24h to a surface dry condition. For new concrete mixed with SRA, the mix composition is shown in Table 2.

### Table 1

<table>
<thead>
<tr>
<th>Cement</th>
<th>Water</th>
<th>Sand</th>
<th>Aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>383</td>
<td>220</td>
<td>792</td>
<td>968</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Cement</th>
<th>Water</th>
<th>Sand</th>
<th>Aggregate</th>
<th>SRA</th>
</tr>
</thead>
<tbody>
<tr>
<td>383</td>
<td>213</td>
<td>792</td>
<td>968</td>
<td>7</td>
</tr>
</tbody>
</table>

The Eclipse Floor, which is a widely used commercial SRA in construction industry, was used in this study [32,33]. Rather than functioning as an expansive agent, the Eclipse Floor acted by reducing the surface tension of pore water. According to recommendations from the literature and the manufacturer, the amount of 7.5L/m³ was used in concrete mixing to obtain optimum performance, and an equivalent volume of water was reduced from the design mix. It should be noted that the water-to-cement ratio was reduced by just 0.01 with this water reduction, which could be regarded as negligible.

Two types of interface were prepared, i.e. smooth interface and rough interface, to investigate the effect of interfacial roughness on interfacial fracture toughness. For the group of rough interfaces, to make sure that the roughness could be regarded as consistent for all the samples, the cut side surface of old concrete was prepared prior to strengthening by creating the grids with a depth of approximately 3 mm, as shown in Fig. 1 (b) and (c). Moreover, before bonding to new concrete, the Teflon taps were attached to the edge of surface with the size of 100 mm × 30 mm to create the pre-crack of new-to-old concrete beam.

After preparation of the old concrete, the old concrete prisms were left in a side of mold and fresh concrete was directly cast on the old concrete interfaces. After 24h, the concrete specimens were then demolded and cured at 20°C with water bath for 28 days.

2.2. Moisture duration

A total of 36 new-to-old concrete beam specimens were prepared, and three factors were investigated in this study, namely the effect of SRA, environmental moist condition and interfacial roughness. A summary of casted samples is shown in Table 3. For the sample names, the first letter, S or R refers to the interface type, smooth or rough. The second letter, S or N, refers to the mix composition of new concrete, with or without SRA, and the third number refers to the time of moisture duration. For each group, three specimens were tested to capture the standard deviation.

For the specimens under dry condition, after 28 days of curing, the new-to-old concrete specimens were put in an air-dry condition in the lab for one month before conducting the test. For the specimens under moist condition, after 28 days of curing, the new-to-old concrete...
specimens were conditioned at 50 °C oven-dry for three days to get rid of free water, and then kept in a water bath condition with focus on the interfacial area. The duration setting is in accordance with previous studies, which indicated that the water absorption rate of concrete decreases from initial exposition to 20 days of water duration, and the water absorption as well as the degree of saturation were kept at a relatively constant level with a marginal increase after 20 days. Hence, 2 weeks and 4 weeks of water duration were chosen in this study as representative duration [31,34].

According to the compressive test of the concrete cube, the compressive strength of new concrete mixed with and without SRA varies from 47.6 MPa to 47.1 MPa and from 49.5 MPa to 48.2 MPa, respectively, after 4 weeks of moisture conditioning. The elastic modulus of old concrete, new concrete mixed with SRA and new concrete without SRA is determined as 32.9 GPa, 32.5 GPa and 32.8 GPa, respectively. Since the deviation is negligible, the average value is taken to calculate interfacial fracture toughness.

2.3. Four-point test set-up and instrumentation

According to the specimen geometry and bonding character, four-point bending fracture tests were adopted in this study, which is an appropriate test method to minimize the plasticity around crack tip before failure [29,31,35]. After conditioning the specimens for the designed duration, all the new-to-old concrete specimens were dried in room condition before testing. All new-to-old concrete specimens were tested monotonically until failure using a four-point bending test with a load span, S, with a length of 100 mm and a support span, L, with a length of 350 mm. The specimens were tested under displacement control at a rate of 0.003 mm/s. Two Linear Variable Displacement Transducers (LVDTs) were placed at the mid-span of both sides to monitor the mid-span deflection.

2.4. Interfacial fracture toughness of new-to-old concrete interface

To investigate the fracture characterization of the biomaterial interface, Dundurs’ elastic mismatch parameters $\alpha$ and $\beta$ are used to describe the mismatch of material properties. The parameter $\alpha$ measures the mismatch of the elastic tensile modulus while $\beta$ measures the mismatch in the in-plane bulk modulus [36,37]. In-plane strain, $\beta$ equals $3/8\alpha$ when the Poisson’s ratio is taken as 0.2 for most cementitious materials. The phase angle, $\Psi$, can be calculated according to the elastic mismatch parameters as well as the geometry of specimens, and it ranges from $-3^\circ$ to 0.52° according to the calculation, which could be considered to be mode I fracture in this study. The experimental set-up for measuring the interfacial fracture toughness through the four-point bending test is shown in Fig. 1 (a) schematically. A pre-crack with a depth of 30 mm was made by Teflon tap before bonding new concrete to old concrete. As a quasi-brittle material, concrete does not behave like linear elastic. Equivalence studies have been conducted experimentally and numerically, comparing the value of fracture parameters from non-linear fracture methods and linear elastic fracture methods (LEFM). The results show that when the sizes of samples are in the range of 150–500 mm, the discrepancy of fracture parameters between non-linear fracture methods and LEFM is negligible. Since the dimension of specimens in this study falls into the above range, the LEFM is adopted to calculate the variations in the interfacial properties of new-to-old concrete specimens.

The mode I stress intensity factor $K_I$ can be expressed as [38]:

$$K_I = f_1 \sigma \sqrt{a}$$  \hspace{1cm} (1)

where $f_1$ is the geometrical correction function according to the relative crack length ($a/h$), $\sigma$ is the length of pre-crack, and $\sigma$ is the stress induced at mid-span, which can be calculated as:

$$\sigma = 6M/bh^2$$  \hspace{1cm} (2)

$$M = P(L - S)/4$$  \hspace{1cm} (3)

where $M$ is the applied moment according to the ultimate load, $P$, for each new-to-old concrete beam specimen, $S$ is the length of load span, $L$ is the length of support span, $b$ and $h$ are the width and depth of the concrete beam, respectively. For the geometrical correction function, $f_1$, when the relative crack length ratio $a/h \leq 0.6$, the following formulas could be used for crack located in the pure bending case [38]:

$$f_1 = 1.122 - 1.4\left(\frac{a}{h}\right) + 7.33\left(\frac{a}{h}\right)^2 - 13.08\left(\frac{a}{h}\right)^3 + 14\left(\frac{a}{h}\right)^4$$  \hspace{1cm} (4)

The corresponding mode I fracture energy release rate can be calculated as:

$$G = \frac{K_I^2}{E_I} = \frac{f_1^2 \sigma^2 \alpha}{a}$$  \hspace{1cm} (5)

where $E_I$ is the Young’s modulus of concrete for plane strain condition, which could be expressed as $E_I = E_I(1 - \mu_I^2)$, and $\mu_I$ is the Poisson’s ratio of concrete. The Poisson’s ratio is taken as 0.2 for all the concrete materials and treated as unaltered throughout the experiment [29,35].

3. Molecular dynamics simulation

The mechanical performance of the new-to-old concrete system
under moisture effect is characterized by macroscopic experiments. Meanwhile, the mechanism of durability difference under moist condition is probed using MD simulation, which can provide detailed molecular-level understanding on the role of SRA in influencing the interfacial properties.

The adhesive mechanism between old concrete substrate and new concrete overlay is related to the mechanical force coming from the cement hydration products of new concrete that are growing into pores of substrate, van der Waals forces and chemical forces acting at microscale, which are responsible for the embedding action between the reactive matrix materials of new concrete repair and the substrate of old concrete [39]. According to previous studies, the induced free water from the environment can significantly reduce the mechanical properties of cement hydration products as well as the van der Waals force, which will reduce the durability of new-to-old concrete system during its service condition [1,30]. The environmental water can penetrate into the interface and influence the interfacial bond as well as the properties of cement hydration products at OTZ. To explore the mechanism of the effect of SRA on water diffusion at the new-to-old concrete interface, MD simulations are conducted.

The multiscale understanding of the structures and components at OTZ has been explored and reported in previous studies. For microstructure at new-to-old concrete interface, it contains C–S–H matrix, portlandite and ettringite at the side of new concrete [39–43]. The multiscale presentation of the structures at new-to-old concrete interface has been confirmed by many researchers using scanning electron microscopes (SEM) or atomic force microscope (AFM) [44–47]. Moreover, for the SRA in pore structures, according to previous studies, a significant fraction of SRA has been found to be immobile and does not diffuse in leaching. This immobile SRA is trapped in gel pore and absorbed on the surface of hydration products through hydrogen bonding of the polar moieties with silanol groups and/or aluminol groups, due to its amphiphilic nature, which has been reported in previous research [48–51]. Hence, a multi-scale model for new-to-old concrete interface containing SRA has been built considering the literature on structure of OTZ and SRA in pore structures, which is shown in Fig. 2.

The major and most important hydration product in the cement matrix is calcium-silicate-hydrate (C–S–H) gel, which has a multi-scale porous structure in which water and ions can diffuse [52,53]. The motion of water in C–S–H gel directly affects the cohesion of C–S–H gel, determining the strength, creep, shrinkage, and chemical and physical properties of cementitious materials [52,54] (concrete, mortar, etc.). In order to investigate the effect of SRA on water diffusion at new-to-old concrete interface, the C–S–H gel model and SRA have been constructed first. According to existing studies on C–S–H gel, the C–S–H model is constructed based on crystalline calcium silicate hydrates, such as tobermorite [53,55]. Tobermorite has the chemical formula Ca₅Si₆O₁₆(OH)₂⋅7H₂O [42]. In this work, the tobermorite supercell cleaved in the [001] direction with a size of 4.0nm × 3.3nm × 2.5nm is constructed as shown in Fig. 3(a). The molecular formula of the commercial SRA is shown in Fig. 3(b). The amorphous structure of SRA with a size of 4.0 nm × 3.3 nm × 2.8 nm is constructed by the Amorphous Cell module in Materials Studio with a density of 0.925 g/cm³ [56].

The structures where water molecules are confined between different layers are modeled to investigate the interaction between water and the C–S–H gel at the interface with and without SRA as shown in Fig. 3 (c)-(e). According to previous studies on the pore structures and diffusional properties of concrete, the C–S–H gel pores in nanoscale (from 3 nm to 10 nm) take most of the pore volume in concrete (with more than 50% volume fraction) [57–59]. Hence, a typical diameter, 6.5 nm, for the C–S–H gel nanopores in concrete to construct the model for simulation, and the set-ups for such a water size are widely adopted in relevant MD simulations in investigating the water diffusion.
properties of cementitious materials (concrete, mortar cement, etc.) [52,54,60,61]. The number of confined water molecules in the inter-layer water region is assumed to satisfy the density of aqueous solution under ambient conditions, namely 1 g/cm³. The cutoff distance is set to 1.25 nm for the van der Waals and Coulombic interactions. The system firstly undergoes a 1-ns equilibration in an isothermal-isobaric ensemble (NPT ensemble), with pressure and temperature controlled by a Nose-Hoover barostat at 1 atm and a Nose-Hoover thermostat at 300 K, respectively. At the end of the 1 ns simulation, the room-mean square displacement (RMSD) of silicon atoms becomes stable, indicating that the system has reached equilibrium state. Finally, the 1 ns NPT running continues after the system equilibrium is reached. Every 0.5 ps, the configuration information is sampled so as to analyze the equilibrium dynamics trajectory.

The reactive forcefield (ReaxFF) has been applied to describe atom interactions. ReaxFF is an empirical forcefield based on bond order relationship that can provide accurate descriptions of bond breaking and bond formation [62,63]. Other valence terms present in the forcefield such as angle and torsion, are defined in terms of the same bond orders so that all these terms go to zero smoothly as bonds break [59]. The non-bonded interactions, namely the Coulomb and van der Waals force between all atoms are screened by a taper function computed for all the atoms [50]. The ReaxFF can provide a good description of the structure, reactivity, and mechanical properties of the chemical systems [52]. The ReaxFF has been successfully utilized in analysis of silica-water interface, C-S-H gel and hydrocarbon oxidation [52,63,64]. The parameters of the forcefield for Ca, Si, O, H and C can be directly obtained from previously published reference data [62,65].

4. Results and discussion

The bond properties of the new-to-old concrete system are characterized by interfacial fracture toughness, which acts as a parameter to quantify the resistance against crack initiation. In order to discuss the bonding properties only provided by adhesion and cohesion of cement hydration, and by both adhesion and cohesion of cement hydration and mechanical interlock, the results from the smooth interface and rough interface are discussed individually.

4.1. Effect of moisture on new-to-old concrete with smooth interface

The typical failure modes of the new-to-old concrete beam specimen with and without moisture conditioning are shown in Fig. 4. In the dry case, the new-to-old concrete beam with new concrete mixed with or without SRA shares the same failure, as shown in Fig. 4 (a), for specimen SN-0. In general, the crack propagated along the new-to-old concrete interface and new-to-old concrete specimens exhibited a new/old concrete interface separation. However, a small number of cement particles that adhered to the old concrete interface can be found for both specimens with new concrete mixed with or without SRA. The specimens with new concrete mixed without SRA under 2 and 4 weeks of moist conditions, exhibited a clear interfacial separation. The cracks
did not kink into new concrete at all during the entire test process, but continued propagating along the moist new-to-old concrete interface, which is shown in Fig. 4 (b) for specimen SN-4. The presence of SRA did not influence the failure modes significantly.

The variation of mode I interfacial fracture toughness under different period of moist condition for the specimens mixed with and without SRA is shown in Fig. 5. For each moist condition, the corresponding calculated fracture toughness is the average value taken from three tested specimens. For the specimens with new concrete without SRA, the interfacial fracture toughness, $\Gamma$, is calculated as $3.24 \, J/m^2$, $2.14 \, J/m^2$, and $0.98 \, J/m^2$, for 0, 2, and 4 weeks moisture duration, respectively. It is shown that a decrease in the interfacial fracture toughness and an asymptotic behavior with the increasing time of moist condition, which means that the continuous moisture ingress can significantly influence the interfacial properties with attack of free water. The interfacial fracture toughness decreased by 34% and 70% for the specimens mixed without SRA conditioning in a water environment for 2 and 4 weeks compared to the interfacial fracture toughness of specimen in dry case. It is observed that such decrease in fracture toughness is associated with the mild shift of the failure mode.

For the specimens with new concrete mixed with SRA, the interfacial fracture toughness, $\Gamma$, is calculated as $3.62 \, J/m^2$, $2.52 \, J/m^2$, and $1.27 \, J/m^2$, for SS-0, SS-2 and SS-4, respectively. A relatively constant decrease rate in terms of interfacial fracture toughness can be found with the increasing duration of moist conditions. The interfacial fracture toughness decreased by 30.3% and 64.9% for the specimens mixed with SRA conditioning in a water environment for 2 and 4 weeks, compared with the interfacial fracture toughness of specimen in dry case. It is observed that compared with the specimens with new concrete mixed without SRA, the decreasing rate in the specimens with SRA is relatively slower. Moreover, by incorporating SRA into the new concrete design mix, the interfacial fracture toughness increased by 10.5%, 15.1% and 22.8% for 0 weeks, 2 weeks, and 4 weeks of moisture conditioning, respectively. These results could be related to the fact that by using SRA in design mix, the shrinkage of new concrete can be reduced as well as the residual stress induced by incompatibility between old and newly cast concrete at interface. During the drying process, the drying shrinkage of concrete can develop significantly due to the loss of capillary water [27,50,66]. The water evaporation from capillary pores results in autogenous stresses and strain within the solid framework of the hydrating cement paste [33]. Because the stresses in pore solution are directly proportional to its surface tension, SRA, which lowers the surface tension of capillary water, can mitigate the drying shrinkage of new concrete and reduce the residual stress at new-to-old interface due to the constraint provided by old concrete. Due to the drying shrinkage, the fracture toughness of new-to-old concrete is reduced during the drying process, and since the usage of SRA can reduce the drying shrinkage, the fracture toughness of specimen with new concrete mixed with SRA is higher than that of normal concrete. Moreover, the SRA can also help to reduce microcracks at new-to-old concrete interface due to residual stress and capillary stress during the drying process, which can further improve the durability of new-to-old concrete specimens in moist environments [23]. Moreover, such residual stress at interface can further induce microcracks in the overlay transition zone given that the mechanical properties of OTZ are much lower than that of bulk concrete material. Another distinctive finding is that with longer moisture duration, the improvement in terms of the interfacial fracture toughness becomes even larger when SRA is adopted in new concrete, which indicates that SRA can improve the durability of interfacial properties of a new-to-old concrete system under moisture attack. This phenomenon could be related to another function of SRA, which is to recede sorptivity and moisture diffusivity when adopted in cementitious materials. With a lower sorptivity and moisture diffusivity, the free water from the environment would penetrate more slowly into a new-to-old concrete interface, resulting in the improvement of interfacial properties and durability for a new-to-old concrete system.

4.2. Effect of moisture on new-to-old concrete with rough interface

In engineering practice, before bonding the new concrete repair material, old concrete surfaces are usually disposed to be roughened in order to achieve better bonding performance. Since the effect of different interfacial roughness has been studied comprehensively in previous research [67–69], the discussion in this part focuses on the effect of moisture and SRA on the interfacial properties of new-to-old concrete with roughened interface. The typical failure modes of the new-to-old concrete beam specimen with and without moisture conditioning are shown in Fig. 6. In the dry case, bending beam specimens exhibited failure in new concrete itself, rendering a cohesive type of failure. The crack propagated into new concrete upon reaching the peak load, and the specimens were failed by concrete delamination for both specimens with and without SRA. Even bulk new concrete was found to be attached to the interface (see Fig. 6(a) for specimen RS-0). Both the specimens with new concrete mixed with SRA under 2 and 4 weeks of moist conditions, and specimens with new concrete mixed without SRA under 2 weeks of moist condition exhibited combined failure mode of adhesive type and cohesive type. The cracks linked between new-to-old concrete and new concrete itself, and the failure surface followed the
shape of a pre-made rough interface, as shown in Fig. 6 (b) for specimen RS-2. This mutative shift in crack propagation tendency is attributed to the fact that moisture ingress and diffusion process at interface is not even, leading to different deterioration degrees of constituent materials and interface. For the specimens with new concrete mixed without SRA under 4 weeks of moist conditions, an interfacial separation can be found, as shown in Fig. 6 (c) for specimen RN-4. The roughness of the old concrete interface can be seen with a relatively small amount of loose new concrete particles attaching to the old concrete interface.

The variation of mode I interfacial fracture toughness under different period of moist conditions for the rough interface specimens mixed with and without SRA is shown in Fig. 7. For the specimens with new concrete without SRA, the interfacial fracture toughness, \( \Gamma_i \), is calculated as 9.62 J/m\(^2\), 6.99 J/m\(^2\), and 4.17 J/m\(^2\), for RN-0, RN-2 and RN-4, respectively. With the interfacial roughness, the interfacial fracture toughness increases significantly compared to the smooth interfacial crack due to involving mechanical interlock in the bonding between new and old concrete. The interfacial fracture toughness decreased by 27.3% and 56.6% for the specimens mixed without SRA conditioning in water environment for 2 and 4 weeks, compared to the interfacial fracture toughness of specimen in dry case. It is observed that this decrease in fracture toughness is slower than that of specimens with a smooth interface. This could be due to the fact that by inducing interfacial roughness, the actual interface area is larger than that of smooth interface.

Fig. 6. Failure modes of new to old concrete beams with a rough interface (a) new concrete delamination of bending beam under dry condition for specimen RS-0, (b) mix mode of concrete delamination and interface separation bending beam with new concrete mixed with SRA after 2 weeks moist conditioning and for specimen RS-2 (c) clear interface separation of bending beams after 4 weeks moist conditioning for specimen RN-4.

Fig. 7. Mode I interfacial fracture toughness of new to old concrete beam specimens with rough interface under different durations of moist condition.

4.3. Molecular dynamics simulations on water diffusion coefficient

As the mean square displacement can effectively characterize the migration path of molecules, it has been proven to be efficient in predicting diffusion coefficients and the diffusion coefficient of a particle undergoing random motion can be given by Refs. [70,71]:

\[
D = \frac{1}{2d} \lim_{t \to \infty} \frac{d}{dt} \left< |r(t) - r(0)|^2 \right>
\]

(6)

where \( D \) is the diffusion coefficient, \( d \) is the dimension of the system, \( r(t) \) represents the particle position at time \( t \). The quantity is the particle mean squared displacement and it grows linearly with time for sufficiently large values of \( t \). For a system with \( N \) particles, the diffusion coefficient can be expressed by Ref. [70]:

\[
D = \frac{1}{N} \sum_{i=1}^{N} \frac{d}{dt} \left< |r_i(t) - r_i(0)|^2 \right>
\]
The diffusion coefficient of confined water in different systems at 300 K. The linearity of MSD plot divided by six is equal to 3. Least-squares fitting can be applied to estimate the slope of curve for the mean squared displacement and time, and D is one-sixth of the slope. The positions of water molecules are determined by the coordinates of the oxygen atoms. Fig. 8 shows the relationship between the mean squared displacement and simulated time. The diffusion coefficient for different regions is shown in Table 4. The diffusion coefficient for each layer computed to capture the nanoconfinement effect provided by the C–S–H or SRA layer, the water layer is divided into three sublayers with same thickness along the thickness direction of the water layer, and the water diffusion coefficient for each layer computed to capture the nanoconfinement effect. The diffusion coefficient, calculated from MSD, reflects the dynamic properties of different water species. The water within 20 Å from C–S–H/SRA can be defined as surface water layer, and the remaining water layer at center or pore is regarded as center water. The diffusion coefficient of surface water near C–S–H and SRA is calculated as 2.11 and 1.01 \((\times 10^{-9} \text{m}^2/\text{s})\), and the diffusion coefficient of center water is 2.9 \((\times 10^{-9} \text{m}^2/\text{s})\). The simulated diffusion coefficients are of the magnitude of the diffusion coefficient of water between the C–S–H particles tested by a proton field cycling relaxometry approach (PFCR) and Time-Resolved Incoherent Elastic Neutron Scattering (QENS), which is within the range of 1/60 \(D_{\text{H2O}}\) and 1/6 \(D_{\text{H2O}}\), where \(D_{\text{H2O}}\) is bulk water diffusion \([72,73]\). Because the PFCR and QENS have been developed to detect the dynamic properties of water molecules adsorbed on the nano-pore surface, the MD simulation results are comparable to those obtained from experiments. The low diffusion rate of surface water near C–S–H should be due to the fact that the water molecules near C–S–H are embedded in the channel and only oscillates around the equilibrium position rather than diffusing randomly and being transported into the bulk water in the central position of pore. For the surface water near SRA, the water molecules tend to interact with hydrophilic head groups of SRA, resulting in a lower diffusion coefficient of surface water layer near SRA. For the reasons above, the diffusion coefficient of water near the surface of C–S–H and SRA is lower than that of the water at the center of pore due to the effect of nanoconfinement. These results indicate that the presence of immobile SRA can reduce the diffusion coefficient of pore water. Moreover, this value is lower than the diffusion coefficient of water in the air. Fig. 9 shows a snapshot of the interfacial structure between SRA and pore water. In both systems where the water is confined in the SRA layers and between SRA and C–S–H gel, the water molecules tend to interact with the hydrophilic head groups (–OH) of SRA and significant nano-roughness is developed near to the compound head groups at the SRA/water interface, resulting in a lower diffusion coefficient of pore water. The results indicate that the presence of SRA can reduce the water diffusion coefficient of nano-pores at new-to-old concrete interface, which improves the durability of the new-to-old concrete system in moist condition. Moreover, although the results from MD simulations provide some fundamental understanding of the initial state of the effect of SRA on new-to-old concrete interface at nanoscale, during the entire service life of such a system, microstructure may change due to the presence of SRA in new concrete. It is reported that SRA can interact with portlandite and generate C–S–H gel under certain environmental condition, which can reduce the pore volume and improve the mechanical properties as well as durability of concrete \([49,51]\). On a larger scale, due to the role of SRA reducing the surface tension of water, it influences the interaction potential energy between capillary walls and helps to reduce the diameter of capillary pores at microscale during the drying process. This could be another benefit provided by SRA in improving the durability of concrete. Hence, based on the insight from MD simulations, more research is needed to link up the fundamental understanding of the effect of SRA at nanoscale to the microstructure changes under different environmental conditions over the entire service life of the new-to-old concrete system. Apart from the simulation methods, a more detailed nanostructure characterization with the help of a more advanced technique, such as Transmission Electron Microscope (TEM) or even in-site TEM test, can illustrate nanostructures and fracture mechanisms more comprehensively. The nanostructure of C–S–H gel pore with and without SRA, fracture surface, fracture process, and even the diffusion process can be captured by these techniques, which can dynamically advance the understanding of the action mechanism of different admixtures in concrete, and their impact on the properties and structures of concrete from nanoscale to microscale.

### Table 4

<table>
<thead>
<tr>
<th>System</th>
<th>MD simulations ((\times 10^{-9} \text{m}^2/\text{s}))</th>
<th>Reference value ((\times 10^{-9} \text{m}^2/\text{s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C-S-H)-water-(C-S-H)</td>
<td>2.86</td>
<td>1.2–3.2 ([74,75])</td>
</tr>
<tr>
<td>(C-S-H)-water-SRA</td>
<td>1.34</td>
<td>–</td>
</tr>
<tr>
<td>SRA-water-SRA</td>
<td>0.54</td>
<td>0.36–0.46 ([26])</td>
</tr>
<tr>
<td>Air-water</td>
<td>–</td>
<td>2.00 ([76])</td>
</tr>
</tbody>
</table>

5. Conclusion

Experimental tests and molecular dynamics simulations were performed to investigate the effect of SRA and moisture on the fracture behavior of a new-to-old concrete bonding system. Experimental tests demonstrate the distinguished fracture modes of different new-to-old concrete samples. The interfacial fracture toughness of a new-to-old concrete system decreases with extension of the duration of moist environment condition. The use of SRA in new concrete can improve the compatibility between new and old concrete by reducing the shrinkage of new concrete. Moreover, it has been found that the use of SRA in new concrete can enhance the durability of a new-to-old concrete system under moist conditions. By performing MD simulations, the effect of SRA on water diffusion in nanopores at new-to-old concrete interface is explored. The water diffusion coefficient can be significantly reduced by adopting SRA in the new concrete design. With a lower rate of water diffusion at interface between new and old concrete, the interfacial properties are improved and more durable performance for the new-to-old concrete system is achieved. The combination of experiments at
macroscale and simulations at nanoscale exemplifies a multi-scale approach, which can be further extended to explore the interfacial properties between other repair materials (such as high-performance fiber reinforced mortar and, self-consolidated concrete or mortar) or admixtures and old concrete structure. Future investigations into the combined effect of SRA, fibers and other admixtures on the bonding properties of high performance concrete (HPC) to old concrete structures are recommended, so that a more sustainable repair and strengthening scheme can be achieved to extend the service life of repaired concrete structures.

Acknowledgments

The authors are grateful to the support from the Research Grants Council (RGC) of the Hong Kong Administrative Region, China [Project No. CityU11255616]. This work was also supported by computational time granted from the Greek Research & Technology Network (GRNET) in the National HPC facility - ARIS - under project ID pa171204-MD- Interface.

References
