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Effect of interfacial transition zone on the Young's modulus of carbon nanofiber reinforced cement concrete

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ABSTRACT

Identifying the properties of the region where the cement paste meets the aggregate surface (interfacial transition zone, ITZ) is critical to understanding the strength and fracture behavior of carbon nanofiber (CNF) reinforced cement concrete. In this study, the finite element method is employed to investigate the effect of the ITZ on the Young's modulus of cement concrete made with CNF. The numerical models for cement concrete with and without CNF are constructed based on the digital image processing technique. To consider the interface effect, the concept of "effective aggregate" is put forward, namely, the Young's modulus and Poisson's ratio for each aggregate particle are replaced by an effective Young's modulus and effective Poisson's ratio, in which the effect of thickness and the Young's modulus of ITZ is taken into account in an averaged manner. Then, the quantitative nanomechanical mapping (based on atomic force microscopy) technique is adopted to measure the Young's modulus and thickness of ITZ with and without CNFs, which are further used as the input parameters in the numerical model. The numerical simulation results are verified by experimental testing, which indicates that the ITZ effect should be considered when implementing the numerical simulation. In addition, this analysis shows that compared with the plain cement concrete, CNFs can greatly enhance the mechanical properties of ITZ, which will in turn improve the Young's modulus of cement concrete significantly. Finally, the effect of thickness and Young's modulus of ITZ on the Young's modulus of CNF reinforced cement concrete is also discussed.

1. Introduction

Concrete is one of the most durable and widely used building materials around the world. However, the shortcomings of concrete, such as low fracture toughness, low Young's modulus, and dimensional instability still limit the use of the material [1]. As nanomaterials have been developed and become more common and affordable, there has been increasing interest in exploring their use as an additive to existing concrete materials. With respect to fiber-shaped nanomaterials such as carbon nanotubes (CNT) and carbon nanofibers (CNF), many studies have shown that mechanical strength properties of cement paste can be improved significantly [1–3].

CNF is an attractive reinforcement for composite materials due to properties such as high strength, high elastic modulus, high aspect ratios, thermal stability, electrical conductivity, etc. [4] The average size of CNF (with a diameter of 50–100 nm) is between microscale carbon fibers (diameter of 7–10 μm) and CNT (diameter of 1–50 nm) [5,6]. However, the mechanical and thermal properties of CNF are superior to carbon fiber, and CNF has a cost advantage compared to CNT [7]. For CNF, the motivation for early studies of nanomodified concrete may have been a conventional wisdom that owing to the success of fiber reinforcement at the meso- and micro-scales in concrete (due to fiber bridging and pullout and other forms of energy dissipation), the same principle could work at the nanoscale and potentially arrest microcrack formation and coalescence. Gdoutos et al. [8] studied the effect of the addition of CNFs on the corrosion behavior, electrical resistivity, and mechanical properties of nanomodified Portland cement mortars. They found that the addition of 0.1% CNF by weight of cement increases both flexural strength and Young's modulus by 110%. Sanchez et al. [9] investigated the mechanism of CNF's effect based on the experiments and molecular dynamics methods. They added 0.5 wt% CNF to cement composites, and claimed a residual effect of the CNF after decalcification of the composites as proved by a slow load dissipation after peak load under compression. Tyson et al. [10] incorporated 0.1% CNT and 0.2% CNF by weight of cement into the concrete, and found that CNF improved performance better due to their higher aspect ratio compared to CNT. Sanchez and Ince [11] pointed out that high content of CNF (2 wt%) can reduce the total volume of accessible pores due to the

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obstruction by the CNF, leading to a greater water penetration resistance.

Constituents in particulate-filled composite materials are usually inhomogeneous, which can lead to the mismatch of properties between granular materials and matrix. It has long been accepted that the mismatch can be mitigated because of the existence of the interfacial transition zone (ITZ) between two components. The study conducted by Scrivener and Nemati [12] proved that the porosity of the cement paste in ITZ, which is higher than that of bulk cement paste, can explain the statement that ITZ has an important effect on the transport properties of cement concrete. According to Olivier et al. [13], the excess of porosity is both the cause and the consequence of the existence of ITZ. ITZ is usually regarded as the weakest zone for mechanical strength in some composites like cement-based mixtures, since it has the higher porosity and less hydrate products compared with the matrix [4–17]. Huang et al. [18] believe that ITZ can reduce the stress concentration between asphalt binder and aggregate, which improves the performance of hot mixed asphalt (HMA) mixtures. Zhu and Chen [17] used a systematic line sampling algorithm to determine the apparent ITZ thickness around regular polygon and ellipse. Their study showed that aggregate shape has significant impact on the ITZ thickness, which can lead to a further effect on the macro-properties of composites. Bosque et al. [19] used nanoindentation and scanning electron microscopy (SEM) to study the properties of various recycled aggregate/paste ITZs and analyzed the influence of ITZ on the performance of recycled concrete. The results showed that the degree of impact of ITZ on the macro-mechanical performance partly depends on the relative content of constituent materials in the recycled aggregate.

It has been well accepted that the ITZ in cement concrete is a region with a higher w/c ratio, and thus a higher porosity. However, nanoparticles, such as nano-silica (NS), CNT, and CNF, can act as individual fibers anchored in the hydration products within the ITZ and thus as entangled networks in cavities [20–22]. Li et al. [23] investigated the microstructures and porosity of ITZ in nano-modified recycled aggregate concrete (RAC) by using SEM and mercury intrusion porosimetry (MIP). Nano-silica (NS) was shown to be more effective than nano-limestone (NL) for improving the microstructure properties and enhancing the mechanical strength of RAC. Palla et al. [24] proved that adding silica nanoparticles (SNPs) to cement concrete can decrease the porosity, sorptivity and water absorption up to 25–40% and meanwhile densify the ITZ. He et al. [25] successfully strengthened the ITZ and enhanced the interface frictional bond strength between polyethylene (PE) fibers and cement-based matrix by coating CNF on surface of PE fibers through hydrophobic interactions. Their research shows that CNF are capable of filling nano-pores and bridging nano-cracks, which can result in denser microstructure and higher crack resistance of ITZ. Prior research shows that nanomaterials have remarkable impact on the microstructure and mechanical properties of ITZ, leading to the enhancement in mechanical performance of cementitious materials. Therefore, it is convincible that the addition of CNF is able to strengthen the ITZ and to enhance the interfacial bond between aggregate and cement paste [26].

Owing to the significant effect of ITZ on composites properties, numerous researchers took the ITZ into consideration while building analytical and numerical models to predict material behavior. The finite element method (FEM) is a common tool to simulate the performance of concrete [26–29]. Huang et al. [18,30–31] developed an analytical model of three-layered HMA mixtures with the ITZ considered, and conducted a simplified finite element analysis to examine the stress distribution in the ITZ, which was successfully validated by the laboratory experiment. Unlike the assumed homogeneous ITZ model developed by Huang et al., Dridi [32] used a three-phase composite sphere model to describe the microstructure of concrete, where the phase distribution was assumed to change as a function of distance from aggregate surface. Chen et al. [33] employed the generalized self-consistent approach to obtain the equivalent matrix composed by the aggregate, cement and ITZ with multilevel homogenization procedures. The proposed homogenization model was proved to be capable of predicting the properties of concrete. Zhu et al. [34] proposed a micromechanical analytical model to predict the modulus of asphalt concrete, where the thickness of ITZ was neglected and the effect of ITZ was treated as spring with constant stiffness. Bernard and Kamali-Bernard [16] developed a 3D finite element model to investigate the influence of ITZ on the compressive strength and the effective diffusion coefficient of mortar. The influence was explained by the decrease of the porosity in the bulk paste to counterbalance the increase of the porosity in the ITZ. Sun et al. [35] developed a cement mortar-ITZ-one aggregate model to computed the elastic properties of a concrete composite based on the differential effective medium theory (D-EMT). The Mori-Tanaka (MT) model, originally concerned with calculating the average internal stress in the matrix of a material containing precipitates with eigenstrains, is nowadays one of the best known analytical approaches to determine the effective material constants of composite materials [36, 37]. Actually, MT method is on the basis of micromechanics. After using MT model, one can get the effective material constants such as Young's modulus of composite materials. However, the classical Mori-Tanaka method does not consider the interfacial effect. Recently, there are some modified Mori-Tanaka methods, which have considered the interfacial effect, such as the method discussed in refs. [37,38]. However, the modified Mori-Tanaka methods usually treat the interface by a spring layer model or a nonlinear cohesive model, and the parameters of these interfacial models are usually difficult to be measured, which makes it also unrealistic to link the real interfacial condition to the macro-mechanical behavior of composites.

Since the thickness of ITZ is usually considered as tens of microns (basically around 10 to 30 μm), it is hard to build an FEM model of ITZ because of its small size compared with aggregates, as well as the difficulties in mesh generation and accuracy control. So far, few researchers have successfully measured the properties of ITZ which are supposed to be used as the input parameters of numerical simulations. Hence, the existing numerical models are not capable of reconstructing the ITZ to investigate its impact on the performance of cement concrete. Few studies have been found to discuss the mechanism of CNF-reinforced cement concrete, and especially the CNF-reinforced mechanisms in ITZ. Therefore, in the present study, the effective aggregate model, which can not only consider the ITZ effect but also simplify the modeling process, will be developed first. The advantage of this model is that it can link the real interfacial condition to the macro-mechanical behavior of cement concrete. Then, the cement paste, cement mortar, and cement concrete samples with and without well dispersed CNF (0.1% by cement weight) were prepared and tested. The Young's modulus and thickness of ITZ between aggregate and cement paste with and without CNF were measured based on the Quantitative Nanomechanical Property Mapping technique. After that, the measured ITZ properties were used as the input parameters to implement the finite element method based on our proposed "effective aggregate model". Finally, the effect of the Young's modulus of aggregate and cement mortar, as well as the properties of ITZ on the Young's modulus of cement concrete was discussed.

2. Model developments

2.1. Interphase model and spring layer interface model

Two most commonly used models have been put forward to simulate the interfacial zone. One is the interphase model, see Fig. 1(a), described by a thin layer of a third material with specified thickness embedded between matrix (cement mortar) and inclusion (coarse aggregate). This model is quite close to the real situation, since a narrow region with fewer cement particles but more water does exist around the aggregate. This region is called the interfacial transition zone (ITZ).