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Nano-engineering of construction materials using molecular dynamics simulations: Prospects and challenges

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ABSTRACT

In recent years, research articles involving molecular dynamics simulations of construction materials have grown significantly in number. The growth reflects an emerging need to understand microscopic physical and chemical processes, which are fundamental to further improve the macroscopic performance of construction materials. Nano-engineering, as a concept about manipulating material structures for creating new materials or modifying existing materials, highly depends on the understanding of materials at the nanoscale, where molecular dynamics simulation becomes an effective and powerful investigation tool. In this paper, the applications of molecular dynamics simulations in understanding the fundamental deformation mechanism of various construction materials including concrete and cement, fiber-reinforced polymers and related bonded systems upon nano-engineering approach are presented. In addition, the study on nature materials towards their structural morphology and functions at the atomistic level is illustrated so as to inspire the future development of advanced construction materials. The challenges and innovations associated with nano-engineering are also discussed.

1. Introduction

The breakthroughs in nano-engineering over the past few decades enable investigations upon intricate phenomena in material systems at the nanoscale, which contributes to the development of strengthened materials with unique features. As construction materials are closely related to our daily lives and people become more aware towards sustainability, their mechanical behaviors, especially durability, become the key concern. It has been reported that most of construction materials look good when only focusing on their performance in a short term, but they can significantly deform or even fail upon external loadings (which is within its designed capability) in natural environments over a certain period of time due to the deterioration within materials or the interaction between materials and surroundings [1–3]. The material deformations always originate from the atomistic scale, which are hardly noticeable using traditional techniques including existing experimental detection and continuum theory. Such an obstacle has hindered the advancement of construction materials in the past few decades until the nano-engineering concept (through simulations) has emerged as an effective approach, which can really break the ice for the research field of construction materials. In the past few years, such simulation approach has been developed significantly in response to the increasing demand for enhancing construction materials with satisfactory performances and delayed degradations. More importantly, the use of nano-engineering in the field of construction materials can help us discover various fundamental failure mechanisms inside material systems and such information provides lots of inspirations for structural design, which is beyond the scope of civil engineering.

The nano-engineering employs the perspective from the nanoscale towards in-depth understanding of underlying properties and deformation mechanisms that govern macroscopic performance of construction materials, and the procedure is implemented as shown in Fig. 1. The modeling scheme using molecular dynamics (MD) simulations for addressing nanostructures and atomistic interactions inside material systems is essential when applying the nano-engineering approach as it is required to evaluate atomistic movements based on material science and inherent behaviors of actual materials. MD simulations serve as effective computational experiments to characterize material properties and predict mechanical responses, which can be used to verify theoretical hypotheses. An earlier development of MD simulation was reported in 1950s for a study on the dynamics of a hard sphere system consisting of several hundreds of particles [4]. Since

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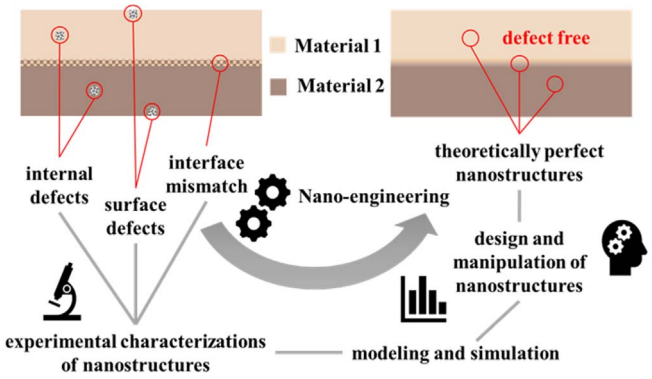

Fig. 1. Proposed implementation of nano-engineering processes for enhancing material properties.

then, the advancement of MD simulation has been observed with the evolution of computational power in the last few decades. MD simulation represents a powerful tool for potential applications in various research fields including physics, chemistry, biology, bio-engineering and medicine [5,6]. Recently, efforts have been made for applying the method to the fields of structural mechanics and civil engineering. Traditionally, the classical continuum mechanics theories have been the basis for most computational methods used in various engineering fields including civil and mechanical engineering; examples are finite element analysis, finite difference method, finite volume and boundary element methods. The capability of the continuum approach is limited when structural solution at a small length scale is of concern. In other words, the predictions about material behavior should be made from a fundamental bottom-up perspective.

In MD simulations, materials can be treated as aggregation of atoms which are regarded as classical (non-quantum and subjected to Newton's Laws of motion) mass particles. This method is based on trajectory of atoms in the modeling system and can provide data that involves time evolution of material nanostructures subjected to external conditions. Basically, the computation involves iterative manipulation of three important parameters including displacement/position, velocity and acceleration as the solution of Newton's second law. To improve the calculation efficiency in the iterative processing, different numerical methods have been developed, for example, Verlet integration, leapfrog integration, velocity Verlet integration and predictor-corrector integration [6]. These algorithms have their own strengths and weaknesses, and are feasible to be employed for different materials. The forcefield plays an important role in describing interatomic interactions, and the selection of forcefield critically determines the validity of MD simulations. A number of widely used forcefields have been introduced for different kinds of material systems [7–10]. These forcefields target for either inorganic or organic polymers, while no direct description for general construction materials is available. The common functional terms including general bonded and non-bonded energies from these forcefields have been adopted in construction materials as the formulation of interactions can be shared in similar structures. For the MD simulations without any chemical reaction, the non-reactive forcefields can be employed to describe the interactions between different components in the material systems. However, the connectivity among components can be altered in special conditions associated with release of atoms as well as generation of new phase (*i.e.* involving chemistry), where the non-reactive forcefields are no longer available. To simulate bond breaking and bond formation in material systems, the reactive forcefield such as ReaxFF [10] can be used. The reactive MD enables the investigations of chemical reaction mechanisms including catalysis, pyrolysis and combustion. The enrichment of forcefields for various interactions satisfies the need of describing the interactions between dissimilar components as well as between materials and external surroundings such as water or other molecules in solvent environments, which cause the structural change in construction materials and affect material properties in a long run. The results generated from MD simulations can provide the key missing knowledge of traditional construction materials at molecular level, which has been usually overlooked for the past few decades.

When applying MD simulations in construction materials research, there are critical challenges covering how to extract information during physical and chemical processes from the nanoscale and to relate the nanoscale information to the macroscopic material performance. Although MD simulations have been widely applied on the study of construction materials over the past few years, this computational approach has a limitation in both the time scale and the length scale. In view of such a small magnitude of time and length scale, which are generally nanosecond (10^{-9} s) and nanometer (10^{-9} m), MD simulations are not suitable for directly studying construction materials as they are always large in length scale and their performance in a long run is always the key for a sustainable design. To resolve the limitation in both the length scale and the time scale, the multiscale modeling for construction materials is proposed that can link MD results to microscopic observations so as to interpret material behaviors. Recent advances in computational power and algorithms have increased the timescales for capturing material behaviors over millisecond-scale. These limitations further motivate the development of applying nano-engineering concept in construction materials.

In this paper, the nano-engineering approach using MD simulations on the studies of construction materials, as well as the recent progress on the fundamental understanding of construction materials and their behaviors, is reviewed with an emphasis on the linkage between the nanoscale and the macroscale, and the transition from research to practical applications. Widely used construction materials like concrete, fiber reinforced polymer (FRP) and their related bonded structures are selected as representative material systems here. For the selected material systems, atomistic modeling, forcefield selection and simulation details under different conditions are introduced and evaluated. MD simulations demonstrating how physical and chemical processes behind macroscopic material performance are presented. In addition, the state-of-the-art related to bio-inspired materials provides a new insight towards the future research direction for construction materials. It is envisioned that the development of construction materials should be founded on the active learning from the natural features of biomaterials. The crucial challenges of nano-engineering approach using MD simulations are also addressed, which are important for our future research and development. This review demonstrates the capability of nano-engineering for research of construction materials, which is a breakthrough from the traditional idea which normally sticks to the investigations of construction materials using macroscale models only to an innovative approach which integrates two extreme and disconnected fields (*i.e.* discrete versus continuum) as a whole. The comprehensive knowledge of the existing research findings and the clear understanding upon the limitations can accelerate the progress of nano-engineering for construction materials.

2. Concrete and cement

As a complex composite, concrete consists of a binding phase (cement matrix) and a particulate phase (aggregates). In normal strength concrete, the particulate phase is much stronger than the binding phase. Therefore, mechanical properties of concrete largely depend on the cement matrix. In this composite material system, the cement matrix is the key focus of MD simulations, which contains four major components as shown in Fig. 2. All of these components react with water to generate hydration products. Nanostructures, hydration processes and mechanical properties of the unhydrated clinkers as well as hydration products are of major interests. Besides the analysis of material structure and basic mechanical properties, the nano-engineering approach is particular useful to facilitate the study of time-dependent behavior and decode the nanogranular origin of creep in concrete [11].

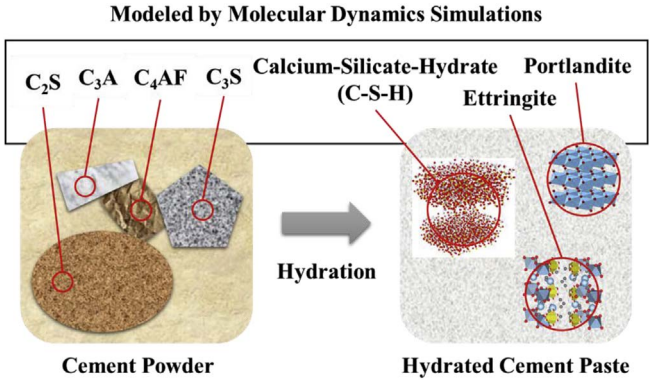

Fig. 2. Important components in cement investigated by MD simulations.

2.1. Cement minerals

Cement material system is reviewed following the bottom-up concept. Atomistic models of cement components are developed based on experimental characterizations. With a proper selection of forcefield, MD simulations can be performed and material properties can be calculated. Understanding material behaviors at the nanoscale paves the way to improve strength and durability of cement-based materials by nano-engineering approach. For example, knowing molecular structures of reactive components in cement clinkers may contribute to searching supplementary cementitious materials (SCM) for sustainability concerns.

Tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetra-calcium aluminoferrite (C_4AF) are four major minerals in ordinary Portland cement (OPC) powder. At the nanoscale, their mechanical and chemical properties can be studied via MD simulations. The starting point of MD simulations lies on the molecular structures of these minerals in crystalline forms, which are often resolved by X-ray crystallography. Another basis of MD simulations is a reasonably accurate forcefield that can describe interactions between atoms of the minerals, which cover calcium, silicon, oxygen, hydrogen, aluminum and iron. Among these minerals, C_3S, C_2S and C_3A have been successfully modeled and simulated. Those reported works are useful references that facilitates model constructions in future MD simulations [12–17].

C_3S, or alite, accounts for around 50% weight of OPC powder. Three kinds of structural families of C_3S are found [12]. A forcefield that can reproduce reasonable surface and interface properties is developed [18], which is compatible with many other commonly employed forcefields. Dissolution mechanisms at crystal surfaces with different cleavages are investigated by ReaxFF-based simulations [19]. Fracture mechanics and reactivity have been studied [6] by using ClayFF potential. This study also includes a comparison among different forcefields and it is shown that ClayFF is a very effective one for large-scale simulations. Hydration of C_3S with substitutional impurities has been studied via density functional theory (DFT) calculations and ReaxFF simulations [20]. At a relatively large scale, MD modeling of cement paste as a two-phase composite system, which includes hydrated and unhydrated phases, is proposed [21]. This model captures heterogeneous features of cement paste and can represent cement paste rationally.

C_2S is also called belite and it accounts for around 20% weight of OPC powder. Five types of C_2S polymorphs are identified as representative models [13,14]. Based on the atomistic structures and the ClayFF potential, MD simulations are performed to characterize crystalline properties of this structurally complex material, C_2S. At the surface of C_2S, electronic structures and adsorption energy surface can be computed via DFT calculations [22]. Behaviors of water molecules can be simulated by using ReaxFF [22]. Effect of polycarboxylate ether-based (PCE) superplasticizer on C_2S substrate is investigated by COMPASS-based MD simulations [23]. Substitution of metal ions at the surface of C_2S is also investigated by DFT calculations and forcefield simulations based on core-shell potential model [24].

C_3A and C_4AF are minor phases in OPC powder. In the past decade, there are some simulations on C_3A and few MD simulations on C_4AF. Structural and elastic properties of C_3A crystals can be found in the existing literature [15–17]. COMPASS, universal forcefield (UFF) and Dreiding forcefield have been evaluated upon its feasibility for cement application [15]. Recently, focal point of MD simulations on cement has been put on hydration products of alite, belite and C_3A. The hydration products are constituents of hardened cement and are closely related to the mechanical performance of cement as well as concrete. Among the hydration products, calcium-silicate-hydrate (C-S-H) is regarded as the most important binding phase.

2.2. Hydration products

Calcium-silicate-hydrate (C-S-H) occupies more than 50% volume in the paste and is a major component of hardened hydrated cement paste. C-S-H provides cohesive force to hardened cement and is regarded as the most important hydration products in cement. Atomistic models of C-S-H are derived from experimental characterizations, which mainly involve water content, Ca/Si ratio, density, tetrahedral coordination of silicate as well as micromechanical tests. Forcefields including COMPASS [9], ClayFF [25], CSH-FF [26] and ReaxFF [27] have been used. The INTERFACE forcefield, an extension of these common forcefields, has also been developed for the interactions at the inorganic-organic and inorganic-biomolecular interfaces [28]. The composition of different phases in C-S-H plays an important role in the structure and mechanical properties [29,30]. Therefore, an accurate model is required in MD simulations for nano-engineering approach. Models derived from tobermorite and jennite are reasonable representatives of C-S-H [31–35]. Based on those pilot works in modeling different constituents within C-S-H, the breakthrough of a full atomistic model for C-S-H has been reported [36]. The success of this realistic model enables the studies on deformation and cracking after loading from the nanoscale, which are historical problems during the service life of concrete, and the detailed atomistic description contributes to the multiscale modeling for C-S-H [37]. Still, there is no stop on the improvement of C-S-H models [38–41]. A colloidal model using spherical particles is applied to probe the multidomain character and mechanical response of C-S-H, which indicates the relationship between packing fraction and elastic properties [42]. The coarse-grained (CG) models are built using disk-like building blocks derived from the associated atomistic model. It is shown that the CG models are more related to the experimental observation and can link up with the macroscopic properties of concrete seamlessly [43,44]. As mentioned before, hydration is significant in C-S-H and the understanding of this process helps to unravel the structure and mechanical properties of cement [45,46]. The hydration of calcium oxide in contact with different amount of water has been studied using reactive forcefield, showing the role of water in remaining the surface structure [47]. Water sorption and shrinkage in C-S-H have also been modeled and the simulation results have been integrated with the experimental results for predicting the long-term property [48]. The hydrophilic nature of the C-S-H nanopore space is revealed and the confined water in the C-S-H affects the structure [49–51]. The reduction in plasticity of C-S-H gels from dry to saturated state has been observed, during which water prevents the reconstruction of bonds between interlayer calcium atoms and silicate chains [52]. The composition-dependent characteristic related to the mobility of water molecules is found [53], while the hardness is also dependent on the composition [54]. The mechanical origin of nanoscale contact, friction and scratch in C-S-H can be understood using MD simulations [55]. The shear response of C-S-H is found to be related to the confined water [56]. Recently, the reinforced structure has been considered for cement by adding extra fibers. The

interactions between fiber and cement matrix have been studied extensively using MD simulations [57].

3. Fiber reinforced polymer (FRP)

The traditional construction materials, such as the aforementioned concrete and wood structural members, suffer from unwanted deformation and degradation when subjected to external loadings at different environmental conditions during engineering applications. To reinforce or rehabilitate these structural components for long-term service, FRP composites have been adopted as ideal candidates due to the advantages of high specific strength and specific stiffness, lightweight, noncorrosive, and easily constructed and tailored to satisfy special requirements [58–61]. The mechanical properties of FRP composites and FRP bonded systems are mainly governed by the interfacial bonding between fiber and matrix, and between FRP layer and substrate materials, which have been measured and evaluated by numerous experimental techniques and numerical modeling approaches. However, the uncertainty still remains regarding the sustainability and durability of the relevant material systems, which are the two main concerns for the design. The existing observations which can detect the macroscopic responses are insufficient to disclose the dominant role of fiber-matrix interfacial characteristics and the underlying mechanism of deformation, and these missing parts appear to be an obstacle to the feasibility of FRP composites used as construction materials. The molecular techniques based on nano-engineering have acted as an attractive alternative again, and shed light on comprehensive and fundamental understanding of nanoscale phenomena. The availability to fabricate and manipulate the atomistic structures of FRP, to capture the interfacial interactions and to yield specific molecular information that can reflect macroscopic properties using MD simulations enables new insights towards the mechanical behavior originated from nanoscale and the design of FRP for proper and unique functions.

Whenever we use FRP, a bonded system is formed and the interfacial integrity becomes critical when subjected to various environmental factors (*i.e.* durability consideration). To start with, when researchers handled this problem, experimental approach with empirical modeling studies were mainly adopted. This approach can help describe the deterioration process quantitatively, yet the associated deterioration mechanism remains an unknown. There is a breakthrough paper published in 2011, which is to introduce the MD simulation to the structural mechanics and engineering field through a fundamental understanding at the atomistic scale and to demonstrate an associated application in structural engineering [62]. Some background on MD simulation has been provided and an organic-inorganic bi-layer system has been analyzed as an application in which structural concrete-epoxy interface under moisture can well be described. Predictions of concrete-epoxy interface behavior is necessary as a basis for structural design and safety in which engineers can implement multi-material solutions such as retrofitting concrete structures using fiber-reinforced polymer materials. Afterwards, another paper about the multiscale modeling approach has been published in 2012 [63]. This paper is one of the important papers demonstrating how the information from the atomistic scale can be transferred to the continuum seamlessly by combining MD simulation and finite element modeling in a hierarchical approach.

In this section, the models for FRP composites and the applications of MD simulations for understanding the structure-property relationship of fiber-matrix interface are reviewed. In addition, the employment of MD simulations to obtain deformation mechanism of FRP bonded interface from nano-engineering approach is illustrated, which is of great concern to the durability and sustainability for applications.

3.1. Modeling of FRP

The molecular models of FRP are based on the hierarchy of the structure and the types of constituents. Typically, FRP composites are

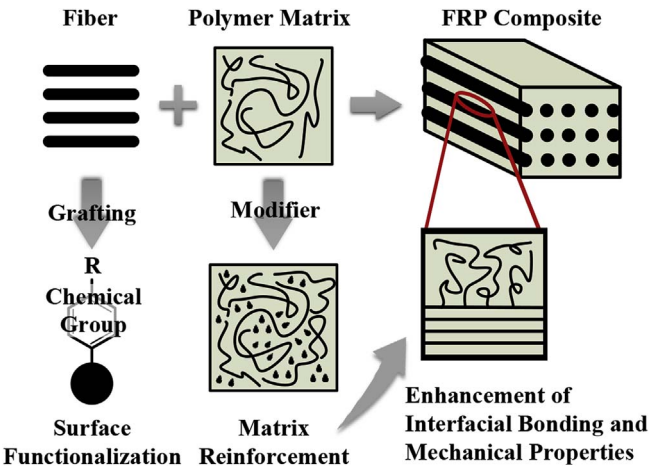

Fig. 3. Schematic layout of FRP composites containing two main components: fiber and matrix. The interfacial bonding between fiber and matrix can be enhanced by surface functionalization and matrix reinforcement for better mechanical properties.

fabricated using a polymer matrix, such as epoxy, and reinforced with various grades of carbon fibers (CF), glass fibers (GF), aramid fibers (AF) or basalt fibers (BF), as shown in Fig. 3. Graphite containing several layers of graphene is the commonly used for modeling carbon fiber [64,65]. The structure of graphene is simple and easy to be manipulated during modeling, in which the effect of material defects can also be considered [66]. These atomistic models enable the simulation on the mechanical performances of fibers during fabrication and application processes. The weight concentration, aspect ratio and dispersion of graphene are found to have an effect on mechanical responses of composites [67]. The thermal properties of graphene-epoxy nanocomposites can also be characterized using MD simulations [68]. As the main component in glass fiber, silica is selected as the basic model for modeling glass fiber [69]. However, the components in aramid or basalt fibers are so complicated that only the basic ingredient is considered in the modeling, such as Kevlar for aramid fibers [70]. The consequently missing information for the full atomistic model of fibers becomes a barrier for the comprehensive nano-engineering on studying the concerned properties. For matrix, the modeling based on the material structures is similar to that of fibers. As thermosetting polymers are usually adopted, the crosslink procedure should be included during the modeling. Different simulation methods have been developed for appropriate construction of the crosslinked structures [71–73]. The crosslink density obtained from different algorithms has an influence on the properties of polymers, as well as on the performances of composites after combining with fibers.

3.2. Fiber-matrix interface

The mechanical performance of FRP composites mainly depends on the compatibility across the fiber-matrix interface, as fibers, matrix and fiber-matrix interface take up the load-bearing during applications. The experimental observations are able to characterize the microstructure of fiber-matrix interface, but the detailed interfacial reactions are unable to be captured and explained solely from the measuring techniques [74]. MD simulations enable the study on the physics of stress transfer through the fiber-matrix interface by capturing the molecular configurations under loading conditions, which tackles the difficulty of implementing the direct experimental measurement. The studies on the FRP composites have addressed several key issues related to the structural behavior of the fiber-matrix interface. From the existing simulation results, the crosslinked density of polymer matrix does not change the interphase thickness, but the density change influences the formation of the interfacial bonding [75,76]. When subjected to external loading, the interfacial debonding and matrix cracking in FRP

composites are the two key deformation phenomena [77]. The initiation and propagation of these two kinds of cracks can be captured by MD simulations.

In addition, nano-engineering from nanoscale perspective aids more detailed consideration upon material design towards the improvement on adhesion between fiber and matrix, and accelerates the evaluation process by modeling and predicting the properties and functions of the resulting composites after treatments through MD simulations, which are time-consuming or hard to accomplish in the experiments. Another method to enhance the bonding between fiber and polymer matrix is surface modification, such as surface grafting with chemical groups [78–80]. The molecular response of fiber-matrix interface after functionalizing the surface of carbon fiber has been investigated [81–83]. It is shown that the modified structure can exhibit a stronger interfacial shear stress. The bottom-up approach to the tailor-made design of FRP composites through special physical and chemical treatments makes great contributions to the optimization process for macroscopic fabrications of FRP.

3.3. FRP-bonded interface

In the strengthened structures using FRP composites, the interfacial bond between FRP and the substrate plays a critical role in determining the performance of the entire system as this region creates the weak link for two dissimilar materials. The interfacial defects affect the long term integrity of FRP reinforced concrete [84]. In addition, the adhesion of FRP bonded regions can degrade when subjected to environmental factors including moisture and temperature [85–91]. The nano-engineering through MD simulations discloses the process of interfacial failure at the atomistic scale, which helps characterize the interfacial behavior and yield the molecular mechanism of deformation. The accurate modeling of the interfacial structure is needed for this bottom-up study. The bonded material system can be represented and simulated by a simple model as the fundamental building block as shown in Fig. 4, which consists of the epoxy monomer diglycidyl ether of bisphenol A (DGEBA) with the key functional group, and the silica substrate. The reason for choosing silica as the substrate material is that concrete consists of different components as described in the previous section, and silica makes up a large proportion of the aggregates. Such simplified model has been applied to investigate the interfacial behavior and understand the physics of adhesion [1,92,93]. The consistent valence forcefield (CVFF) [7] and polymer consistent forcefield (PCFF) [8] are chosen to describe the organic-inorganic interfaces, which have been validated from the previous literature [71,94]. The metadynamics approach (embedded in the MD simulations) bridges the gap between the pulling distances and energy barriers that determines the adhesion energy of the interface [95]. It is found that solvents, such as water and salt, deteriorate the interfacial bond of epoxy-silica system in the wet condition by decreasing the adhesion energy, which is an important factor for evaluating the durability. The simulation results agree with the weakening effect of moisture and salt solution on the performances of FRP-bonded materials from the experiments at the macroscopic level, and provide a molecular explanation for the observations [3,62,94,96,97]. The creep behavior at the interface has also been investigated using this single model, which can illustrate the extension and sliding movement related to two different energy barriers [98]. Considering the crosslinked network of polymer in practical situation, the crosslinked structure of epoxy is developed. A more complicated system is utilized to continue the investigation on the effect of moisture, where a similar detrimental effect on FRP-bonded interface is found [99]. These findings reveal the molecular-level interactions at the interface with the external surrounding conditions, and provide the prediction of the adhesion.

As promising construction materials, wood structural members using FRP for strengthening require detailed testing on the mechanical performances. The interfacial behavior of FRP-wood bonded material system under the effect of moisture has also been investigated using MD simulations [100]. The corresponding CG model for epoxy-wood bonded system in a multiscale study has been developed, which enables the investigation of temperature effect on the structure [2]. Such findings upon the FRP-wood interface decipher the mechanisms of the interfacial debonding and the structural deterioration, and characterize the fundamental origin of deformation that can hardly be captured from the macroscopic perspective. The external loading on the FRP-bonded material systems is another factor that influences the mechanical performances. In consideration of sustained loading, the time-dependent behavior of FRP composites and FRP bonded interface becomes a critical issue in the application [101]. The applicability of MD simulation in capturing the creep response at the interface helps in analyzing the long-term performance in bonded material systems.

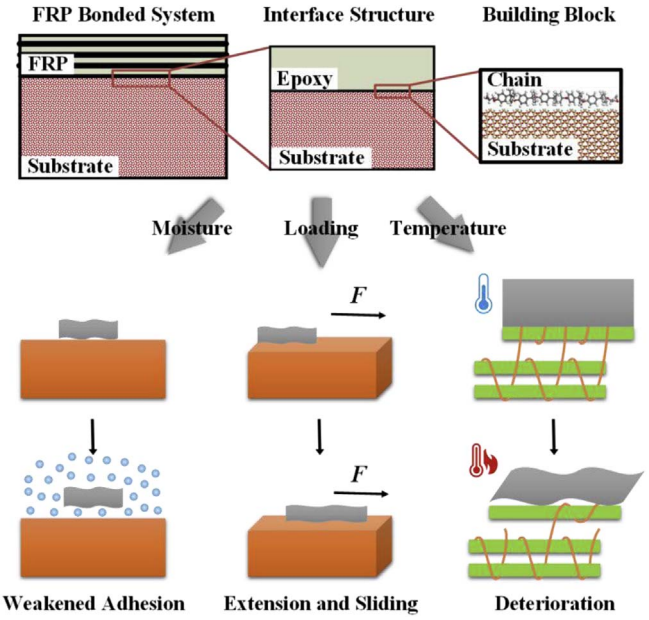

Fig. 4. FRP bonded interfacial structures at different length scale: From macroscale model corresponding to the practical situation, to mesoscale model, and to atomistic scale model acting as the building block for MD simulations. Such approach has been applied to analyze the deformation mechanisms in the conditions of moisture, loading and temperature, which lead to the weakened interfacial adhesion by water molecules, extension and sliding movement of epoxy chain by constant loading, and deterioration of wood structure and epoxy layer at high temperature respectively.

4. Bio-inspired design

The multifunctional properties of natural materials are attributed to their subtle structures derived from the nature, and offer cues for special functions and inspirations for manipulating material structures. Concrete and FRP composites are man-made construction materials, and some inside ingredients are manufactured by artificial synthesis, which can improve the material properties to certain extent while lots of efforts are still required to understand the enhancement mechanism. Natural materials are evolved from adaptation and selection over years, and their inner and outer structures keep developing to resist external damage. These advanced structures from natural evolution can provide insights for designing new materials with special functions, such as radar mimicking echolocation from bats. Materials including molluscous shell and wood that display desirable properties spark the current investigation into bioinspired materials and provide solutions towards challenges in designing strong and tough materials. Learning from natural aspects of these material, people have successfully applied structures originated from plants and insects such as hydrophobic surface and honeycomb wall in coatings, constructions and devices. In recent years, the structural and mechanical response of biomaterials

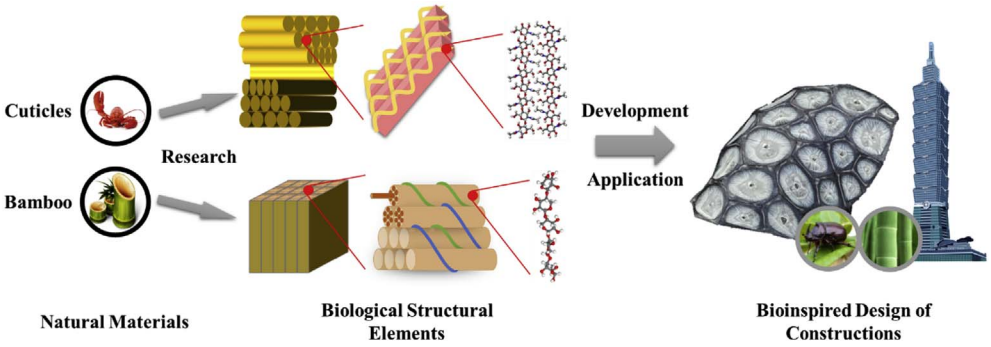

Fig. 5. Proposed work flow of bio-inspired design. The structures of natural materials are firstly characterized in multi-scale using MD simulations, and then the results from research are employed to design structures of man-made materials, such as pavilion imitated fiber orientation from insect cuticles [152] and Taipei 101 imitated bamboo structure. Improved mechanical properties and functionality are envisioned in the development of construction materials.

such as bone and spider silk have been studied [102,103], the results of which have been applied in 3D printing [104,105]. Researchers have used 3D printing technique to produce synthesized materials, which are based on biomaterial structures and possess enhanced material properties. Such engineering skills have been gradually applied on the design and practice in construction industry. The 3D-printed buildings have been practised recently, and the process involves the applications of a powerful 3D printer and suitable materials. Equipped with the nano-engineering approach and the knowledge coming biomaterials, the design of 3D-printed structures with an accurate construction and a less cost becomes feasible in harsh or dangerous environmental conditions where traditional construction methods are no longer appropriate.

To comprehensively understand the features of natural materials, the first step is to characterize mechanical properties and structural behavior. Natural materials possess complex natural structures with different hierarchies, and many investigations have been undertaken to identify and model them [106,107]. The hierarchical structures have enlightened the design for new composites by a combination of different components in special arrangements. To accomplish this progress, the key concern is to extract the basic structure unit at different length scales that can be applied in designing bio-inspired materials or structures for modern engineering demands [108–112]. The nano-engineering approach should be taken as the fundamental as the mechanical behaviors are originated from the molecular level, and this approach can involve the nanoscale features coming from constituent functional groups. The flow of bio-inspired design is shown in Fig. 5. In this section, the studies on biomaterials and wood at the nanoscale are reviewed. Here, MD simulations serve as a convenient tool that can unravel the structural hierarchy inside natural materials which cannot be comprehensively conducted through experimental tests, and the inspiration from nanoscale can be directly employed into structural design, which creates great impact and significance between design and implementation.

4.1. Chitin and chitosan

Chitin and chitosan are natural polymers which are abundant in the constituents of natural chitin-related materials such as lobster, crab cuticles, squid beak and butterfly wings. The modeling of chitin and chitosan is based on the hierarchical structures and experimental observations [113–116]. The forcefields including CHARMM [117] and GROMOS [118] are commonly applied. The MARTINI forcefield is developed for a CG model [119]. Chitin has an affinitive behavior with protein during the application and the interactions of chitin-protein interface are revealed through MD simulations [93]. It is found that the interlocked sites between chitin and protein suffer from breaking under deformation [120]. In addition, the environmental factors, such as water and acidity, have an effect on the molecular structure and interfacial behavior [1,121,122]. The structure of chitin and chitosan inside water has been characterized to find the effective functional group for bonding [123,124]. Considering the acidity issue, the protonation state of terminus plays an important role on the adhesion of protein on the chitin surface [1]. The different deacetylated characteristics of chitin in chitin-based materials cause diverse properties, and thus the effect of acetyl group on mechanical properties of chitin/chitosan nanocrystal is investigated [125]. Based on the structures and the mechanical properties of a single building block, the flexibility of fibrils in chitin structures is found to be affected by the alignment of acetyl groups [126]. The chitin and its derivatives have been used in the design of bioinspired materials [115,127]. The combination of natural and synthetic macromolecules has been applied in the biomedical field, and the mechanical and diffusional properties of chitosan related bioartificial membranes have been investigated for material design [128]. In addition, the ionic crosslinking has an effect on the water state in hydrogel chitosan membranes [129]. From MD simulations, it is found that the incorporation of chitin nanofibrils into chitosan matrix can enhance the mechanical properties of composite fibers [130]. Inspired by these incorporated structures, the construction materials can be strengthened by adding nanofillers for improving mechanical performances, such as carbon nanotube reinforced concrete.

4.2. Cellulose, hemicellulose and lignin

Wood and bamboo are common natural composites used as construction materials because they are light weight and display well mechanical properties. They are made of cell walls mainly consisting of cellulose fibers, lignin and hemicellulose matrix. The modeling of wood and bamboo mainly focuses on these three constituents [110]. The atomistic structures of cellulose, hemicellulose and lignin, and the corresponding CG models are constructed for studying the concerned mechanical behavior [131–137]. The CHARMM forcefield is widely employed in MD simulations [138,139]. As the properties of wood and bamboo are dependent on the structures [140], nano-engineering can unravel the hierarchical structures at different length scales. From the nanoscale, the deformation mechanism of wood has been clearly figured out, which changes from an elastic to plastic manner [136]. The assembly of cellulose and lignin has been investigated using MD simulations, and it is shown that the van der Waals interaction and hydrogen bond interaction mainly contribute to the surface-dependent adsorption of lignin to cellulose [141,142]. In addition, the strong adhesion is caused by van der Waals forces between lignin and cellulose fibrils, while the weak interfaces appear at the amorphous regions of cellulose fibrils [143]. Such findings suggests the molecular origin of strength and stiffness in bamboo. The viscoelastic behavior of bamboo is investigated using MD simulations, which reveals the mechanical origin of the creep response in microstructure [144]. The cellulose nanofibers with superior mechanical properties are found to be good reinforcing fillers for composites [135,145], which is in a good agreement with the existing experimental results [146,147]. Recently, it has been indicated that moisture can affect the elastic moduli of bamboo as water molecules can weaken hemicellulose and lignin [148]. The insolubility of cellulose and the effect of water on cellulose have been investigated [149,150], and the crystalline-amorphous interface of

wood microfibril-hemicellulose system can absorb water, which leads to the weakening in wood [151]. The characterization of these components and the evaluation of their mechanical behavior provide crucial information of the structural properties and functions originated from different hierarchies. The inspiration from wood and bamboo, such as cell wall structure keeping the interior protected, can help in the design of hierarchical building structures for special mechanical performances including stability and stiffness in construction industry.

5. Key challenges in nano-engineering

Although MD simulations on construction material systems have been an active research area over the past decade, some challenges still overshadow the progress in the molecular modeling and the computational prediction. The compositions of construction materials always refer to different physical and chemical components, and the molecular models for these complicated structures in MD simulations are required to correctly mimic the corresponding material systems. For instance, concrete is one of the most complex construction materials, and its constituents with reactions should be included in the modeling process for a realistic representation. The difficulties in accurately constructing atomistic structure for these materials need to be resolved through obtaining more in-depth observations from experiments. In addition, appropriate forcefields which can describe the atomistic interactions inside materials and the bonding conditions between dissimilar materials for targeted systems are still lacking. Without an accurate forcefield, we cannot obtain the actual molecular motions and evaluate the relative properties in practical situations. The specific parameters of interactions between different components require an extensive training using quantum mechanics calculations and experimental validation. To address this issue, some recent improvements have been made on the accuracy of forcefield for specific materials and interfaces [27,153], and more efforts are necessary to comprehend the nano-engineering approach.

As mentioned previously, the spatial and temporal resolutions available in MD simulations does not match with the applications of construction materials, making obstacles for the application of nano-engineering in construction materials. To overcome these constraints, the multiscale modeling from MD simulations at the atomistic scale, to CG modeling at the mesoscale, and to finite element method at the macroscale should be applied to analyze construction material systems. The multiscale modeling facilitates the integration process of the advanced nano-materials with the traditional construction materials effectively. During this process, MD simulations help figure out the optimal size, shape, orientation, distribution and concentration of nano-materials in order to improve the concerned material properties, and unravel the material behavior at atomistic level so as to understand the strengthening mechanisms. Then, the atomistic understanding and predictions can be scaled up to the mesoscale through CG models in the MD simulations. The CG models only reserve the basic molecular structures which simplify atomistic details and are constructed for the connection with analysis in finite element methods for a more recapitulative investigation. In addition, the multiscale modeling is needed in the design for advanced functions of construction materials, which starts from deriving the basic knowledge of specific structure from nano-materials using MD simulations with nano-engineering perspective. Such modeling approach accelerates the fabrication process and eventually leads to new construction materials.

There is a big limitation of MD simulation when applying it to study the long-term performance of material systems. The non-equilibrium state of material systems caused by various external effects requires a relaxation over time for getting an equilibrium state, and such relaxation process is considered as a succession of transitions between local energy minima through pathways from potential energy or free energy landscape. The limitation of time-scale in traditional MD simulations hinders the escape from the local minimum which requires a long relaxation time, and so inhibits the state-space exploration. In recent decades, the application of MD simulations towards long-time behaviors of the materials has become feasible due to the development of two different techniques, including potential energy surface exploration and accelerated approach which can quickly access to the transition-state pathway. The potential surface energy exploration goes over the initial and the final configurations, and then connects with time through the transition state theory. Metadynamics is a commonly used free energy surface sampling technique, which has already been incorporated in software for MD simulations [95]. Especially, the autonomous basin climbing method is proposed to predict long-term mechanical behaviors, and such potential energy landscape exploration has been successfully applied to study the viscosity and glass transition of supercooled liquids and the creep behavior in metals and concrete [154–157]. Such simulation results agree well with the experimental observations. In these methods, well-defined penalty functions are added to the original system to accelerate rare transition events and to find the next minimum energy configuration. Activation relaxation technique and dimer method can also be used to search neighboring local minima in the potential energy surface [158]. Other acceleration approaches, such as parallel-replica dynamics, hyperdynamics and temperature-accelerated dynamics are also wildly applied [158]. In addition, the advance of computational technology and hardware allows us to run simulation programs in a much longer time with large-scale material systems. The extension of these methods for complicated systems and bonded structures of construction materials is necessary for developing promising results on the analysis and predictions of sustainability and durability of materials that can be linked up with macroscale. Furthermore, the steered molecular dynamics has been developed to investigate the responses of the biomaterial systems under the time-dependent external forces [159], and this method can be directly connected with the measurements from microscale measurement technique (*i.e.* atomic force microscope) so as to overcome the time-scale limitation embedded in the MD simulations. These methods and corresponding algorithms help researchers grasp the temporal behavior of construction materials indeed.

6. Conclusions

In this paper, the main progress of nano-engineering approach to construction materials including three different material systems has been reviewed. Nano-engineering, an important approach developed in recent decades with profound impact, has already shown the potential to be the key technology for the next generation of construction materials. In the nano-engineering approach, MD simulations are useful to reveal microscopic physical and chemical processes that underlie macroscopic material phenomena. The accuracy in the modeling of material systems and the choice of forcefields are crucial for nano-engineering using MD simulations, and the progress of developing models for concrete, FRP and bio-inspired composites have been made in a promising direction in the recent decade. The molecular information and deformation mechanisms in these construction materials and associated interfaces with other materials have been revealed through MD simulations. However, the appropriate description of interactions between dissimilar materials are still lacking, which requires more research input with considerations on the detailed microstructures and complicated reactions for future perspectives. The practice of MD simulations in engineering is still in the developing stage because the results at the nanoscale cannot be directly applied in reality in general. The effort of connecting MD simulations in nanoscale and finite element method in macroscale for material research is under way, and it is believed that the impact of such incorporation in different scales will be tremendous. The knowledge of construction materials at the nanoscale can be achieved using nano-engineering concept so that a thorough understanding of their structural properties and mechanical behaviors can be attained. It is envisioned that multiscale models combined with

enhanced simulation methods including descriptions of structures and interactions are really the key for the advancement of construction materials in this century.

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