

Effect of Plasticizer Additives on the Mechanical Properties of Cement Composite – A Molecular Dynamics Analysis

R. Mohan, V. Jadhav, A. Ahmed, J. Rivas, A. Kelkar

Abstract—Cementitious materials are an excellent example of a composite material with complex hierarchical features and random features that range from nanometer (nm) to millimeter (mm) scale. Multi-scale modeling of complex material systems requires starting from fundamental building blocks to capture the scale relevant features through associated computational models. In this paper, molecular dynamics (MD) modeling is employed to predict the effect of plasticizer additive on the mechanical properties of key hydrated cement constituent calcium-silicate-hydrate (CSH) at the molecular, nanometer scale level. Due to complexity, still unknown molecular configuration of CSH, a representative configuration widely accepted in the field of mineral Jennite is employed. The effectiveness of the Molecular Dynamics modeling to understand the predictive influence of material chemistry changes based on molecular / nanoscale models is demonstrated.

Keywords—Cement composite, Mechanical Properties, Molecular Dynamics, Plasticizer additives.

I. INTRODUCTION

CONCRETE, one of the most used materials in the world is a mixture of cement, water, fine and coarse aggregate, and is an excellent example of highly heterogeneous composite material system.

A. Cementitious Materials

Cement paste consisting of starting configuration of dry cement powder and water mixture by itself is a complex, multi-scale composite material system. Though commonly used over the years, cementitious materials are one of the complex material systems in terms of material morphology and structure than fiber reinforced composite materials due to the presence of multiple and highly heterogeneous material phases with no specific repeatability. In addition, cementitious materials undergo chemical and morphological changes gaining strength during the transient hydration process.

Hydration in cement is a very complex process creating complex microstructures and the associated molecular

structures that vary. A fundamental understanding can be gained through nano to continuum multi-scale level modeling for the behavior and properties of both hydrated and unhydrated cement constituents at the atomistic length scale to further explore their role and the manifested effects at larger length scales. Building upon this, this paper focuses on the modeling of key hydrated cement composite material component, Calcium-Silicate-Hydrate (CSH) to obtain their predictive mechanical properties and study the influence of material chemistry changes such as the addition of plasticizer via molecular dynamics (MD) modeling.

Portland cement in the powder form consists of four different major constituents: Tricalcium silicate (C_3S), Di-Calcium silicate (C_2S), Tri-Calcium aluminate (C_3A), and Tetra calciumaluminoferrite (C_4AF) [1]. Different mixture percentage of these constituents produce different types of Portland cement which is the most common used cement [2]. Cement and water mixture (cement paste) is the binder for the concrete, Hydration of cement is the chemical reaction between cement compounds and water, which cause that hardens the cement forming the heterogeneous composite material. The hydration process is highly complex and produces complicated products that control the strength. The most important hydrated cement product is Calcium Silicate Hydrate (CSH). Due to the complexity of CSH, molecular structure of CSH has not been resolved yet. Other naturally occurring minerals Jennite [3] and Tobermorite14 [4] molecular structures are the closest representation of CSH crystal, accepted in the field. Following a Materials By Design paradigm, mechanical properties such as Elastic modulus (E) [5], Bulk Modulus (K) [6], Shear modulus (G) [7], and Poisson's ratio [8] for material systems can be obtained through molecular dynamics modeling of the molecular material structures. These mechanical property predictions based on the CSH Jennite molecular structure via MD modeling and predictive evaluation of the effect of material chemistry changes is the focus of the present paper.

B. Plasticizers

Plasticizers or water reducers, and super plasticizer or high range water reducers, are chemical admixtures that can be added to cement mixtures to improve workability of cement composite. Unless the mix is "starved" of water, the strength of cement paste is inversely proportional to the amount of water added or water-cement (w/c) ratio. In order to produce stronger concrete and cement composite, less water is added

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(without "starving" the mix), which makes the cement paste composite mixture less workable and difficult to mix, necessitating the use of plasticizers, water reducers, super plasticizers or dispersants. This method of mix proportioning is especially popular when producing high-strength concrete and fiber-reinforced concrete. Super plasticizers have generally been manufactured from sulfonated naphthalene condensate or sulfonated melamine formaldehyde, although newer products based on polycarboxylic ethers are now available. Traditional lignosulfonate based plasticizers, naphthalene and melamine sulfonate-based superplasticizers disperse the flocculated cement particles through a mechanism of electrostatic repulsion. In normal plasticizers, the active substances are adsorbed on to the cement particles, giving them a negative charge, which leads to repulsion between particles. Lignin, naphthalene and melamine sulfonate super plasticizers are organic polymers. The long molecules wrap themselves around the cement particles, giving them a highly negative charge so that they repel each other. Polycarboxylate ether superplasticizer (PCE) or just **polycarboxylate** (PC) provide cement dispersion by steric stabilization, instead of electrostatic repulsion. This form of dispersion is more powerful in its effect and gives improved workability retention to the cementitious mix.

This paper employs MD analysis to predict the mechanical properties (Young's modulus, Shear Modulus, Bulk modulus, and Poisson's ratio) of CSH Jennite molecular structure and the associated predictive effect with the addition of plasticizer modifying the material chemistry of the cement composite.

II. METHODOLOGY

Accelrys Materials Studio is a suite of molecular dynamics modeling software, that is used in advanced modeling of various materials (polymers, nanotubes, catalysts, metals, ceramics, etc.) [9]. Molecular Dynamics modeling is a computer simulation of atoms and molecules interacting with each other. MD method was discovered in the late 1950s and early 1960s by Alder and Wainwright[10]. At the present time, MD is applied in modeling materials science and biomolecules, because it can study and investigate the structure and behavior of the interacting atoms at any molecular system. The methodology is based on transient dynamics analysis of atoms represented by system of particles based on classical Newtonian mechanics. The transient dynamic atomistic configurations under varying thermodynamic state conditions is coupled with statistical mechanics to obtain the predicted, thermo-physical properties as well as molecular level behavior of material systems based on the atomistic positions and velocities. The associated Newton's equation of motion can be represented by:

$$F_i = m_i a_i = m_i \frac{dv_i}{dt} = m_i \frac{d^2 r_i}{dt^2} \quad (1)$$

where (m_i, v_i, r_i) are atom mass, velocities, position respectively, F is associated force, defined as the gradient of

the potential energy representing the bonded and non-bonded energy associated with the material's molecular configuration.

The total potential energy for the material system varies for different molecular types because of the change of associated molecular parameters and atoms. The potential energy of the CSH Jennite molecular structure is determined using a COMPASS force field in the present work. The functional form of the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) contains three major terms, which are Bond terms, Non-bond terms, and Cross terms [11]. Bond terms include bond stretch, angel bending, angel rotation, and out of plane angel terms, associated with molecular configuration of the CSH Jennite structure. Fig. 1 presents the bonded atom interaction components in the COMPASS force field/potential energy definition for CSH Jennite. These include bond stretching, angle bending, torsion, and out of plane rotation. Non-Bonded energies include Vander Waals and electrostatic energy as shown in Fig. 2.

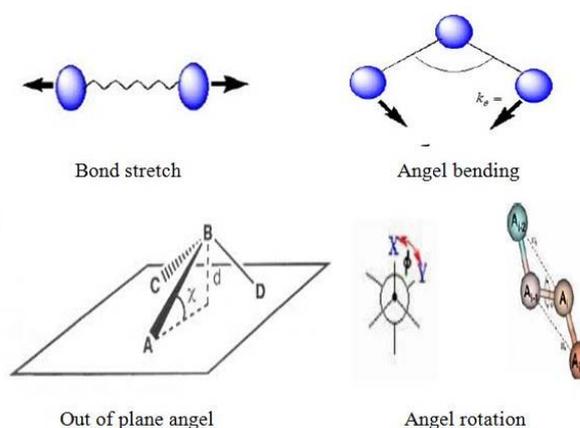


Fig. 1 COMPASS atom bond interaction energy components

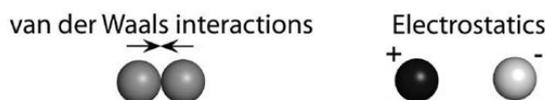


Fig. 2 COMPASS Non-bond Energy Components

In addition, cross terms are important for predicting the vibration frequencies and structural variation, and include the combination of internal coordinates like Bond-bond, Bond-angle, and Bond-torsion.

A. Molecular Dynamics

Molecular dynamics (MD) is a combination of molecular modeling, computer simulation, and statistics mechanics[12]. MD simulation consists of three steps, energy minimization, dynamic simulation, and calculation of the mechanical properties [13]-[15].

1. Energy Minimization

This is to find the stable structure configurations, which corresponds to lowest energy for the molecular system. Some

of the methods that can be used in the static minimization are: steepest descents, conjugate gradient, Newton-Raphson, and simplex method. Steepest descents and conjugate gradient methods are Gradient methods, which depends on the direction of the first derivative, and indicates where the minimum lies. Molecular Dynamics applications use the so called smart minimization method. Smart minimization is a combination of the Gradient and Hessian methods. For systems less than 200 atoms, starting with the steepest descent method, followed by the Conjugate Gradient method and ends with a Newton method. For systems larger than 200 atoms, starting with the steepest descent, followed by the Conjugate Gradient method [9]. This is employed in the present work.

2. Dynamic Simulation

The dynamics of atom motion based on initial velocities that are based on the temperature conditions are determined by solving Newton's equation of motion. The time dependent atom configuration at each time step forms the trajectory with molecular configuration at each time step forming the possible phase state configuration of the molecular system following the principles of statistical mechanics. Time integration algorithms are used to integrate the equation of motion. Some of the time integration methods are Euler Method, 2nd order Runge-Kutta Method (RK2) or sometimes it is called Modified Euler Method, 4th order Runge-Kutta Method (RK4), Verlet algorithm, Velocity Verlet algorithm, and Predictor-Corrector Methods. However, the most commonly used time integration algorithms in molecular dynamics are Verlet algorithm and Predictor Corrector algorithms. The present work employed Velocity-Verlet algorithm. The time dynamic trajectory consisting of several snapshots of atomic positions and velocities of CSH Jennite molecular structure are used for the predictive mechanical property determination in conjunction with Ergodic Hypothesis linking the time average from classical mechanics and phase averages in statistical mechanics.

3. Mechanical Properties Determination

Elastic constants can be determined by the following equation based on the associated potential energy of the molecular system.

$$C_{ij} = \frac{1}{V} \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \quad (2)$$

where $\varepsilon_i, \varepsilon_j$ lattice strain components, U is potential energy, and V is the MD molecular cell volume. The above equation can be used to obtain the Elastic stiffness matrix (C) and the Elastic compliance matrix (S) (the inverse of C) can be determined. Elastic modulus (E) can be computed from Elastic compliance matrix (S)

$$E_x = S_{11}^{-1}, E_y = S_{22}^{-1}, E_z = S_{33}^{-1} \quad (3)$$

Bulk modulus (K) can be computed using Reuss, Voight, and Hill definitions from the elastic stiffness matrix.

$$K_{Hill} = \frac{1}{2}(K_{Voight} + K_{reuss})$$

$$K_{Voight} = \frac{1}{9}(C_{11} + C_{22} + C_{33} + 2(C_{11} + C_{13} + C_{23})) \quad (4)$$

$$K_{reuss} = \frac{1}{9}(S_{11} + S_{22} + S_{33} + 2(S_{11} + S_{13} + S_{23}))^{-1}$$

Shear modulus (G) can be computed using Reuss, Voight, and Hill definitions from the elastic stiffness matrix.

$$G_{Hill} = \frac{1}{2}(G_{Voight} + G_{reuss}) \quad (5)$$

$$G_{Voight} = \frac{1}{15}(C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - C_{12} - C_{13} - C_{23})$$

$$G_{Reuss} = \frac{15}{4(S_{11} + S_{22} + S_{33} - S_{12} - S_{13} - S_{23}) + 3(S_{44} + S_{55} + S_{66})}$$

Poisson's Ratio (ν) which is the ratio of lateral to longitudinal strain can be computed from the following equation:

$$\nu = \frac{3K - 2G}{6K + 2G} \quad (6)$$

4. Periodic Boundary Condition (PBC)

The use of the PBC in MD analysis mathematically helps in predicting the properties of Bulk system employing smaller molecular configurations.

5. Ensemble

Ensemble is a collection of points over time satisfying the same macroscopic or thermodynamics properties used in the MD analysis. Common ensembles in MD are: Micro-canonical Ensemble (NVE), Canonical Ensemble (NVT), and ISOBARIC-ISOTHERMAL Ensemble (NPT). NVE is a fixed number of atoms, fixed volume, and fixed energy. NVE is not recommended for equilibration, but it is good for exploring constant energy configuration. In NVE there is no control on pressure or temperature. NVT is a fixed number of atoms, fixed volume, and fixed temperature. NVT is good when pressure is not a major factor, and when the MD simulation is conducted in a vacuum without periodic boundary conditions. MD analysis employs temperature controlling methods such as Velocity scaling, Berendsen, Anderson, Langevin dynamics, and Nose-Hover. NPT is a fixed number of atoms, fixed pressure, and fixed temperature. NPT is good when correct pressure, volume, and densities are important during the MD analysis. Pressure control is achieved via Parrinello [16], Berendsen, and Anderson control methods commonly used in MD.

6. Time step

Time step is one of the important parameters in MD simulations, because the right choice of the time step value

will lead to stable and accurate results. Time step should be around one tenth of the shortest period of motion of the atoms. A time step of 1 fs (femto second) is employed in most of the MD analysis in the present work.

III. ANALYSIS DETAILS

Based on the above discussions, a summary of the parameters employed in the present work for the MD analysis is presented in Table I.

TABLE I
SIMULATION RUN PARAMETERS

MD Parameters	Jennite	Jennite with plasticizer additive
Cell sizes	1aX1bX1c	1aX1bX1c
Molecular Tool	Forcite -MS	Forcite -MS
Energy minimization	smart	smart
Force fields	COMPASS	COMPASS
MD ensemble	NPT	NPT
Temperature K	298 K	298 K
Temperature control	Nose	Nose
Pressure Gpa	0.0001	0.0001
Pressure control	Berendsen	Berendsen
Time step	1fs	1fs
Dynamics Time	100 ps	100 ps

A. MD Simulation of C-S-H and Plasticizer

The molecular structural configurations for MD modeling of modified C-S-H material chemistry structure with the plasticizer was obtained as follows to emulate the addition of 1% to 2% weight addition of the plasticizer polycarboxylate ether. Based on the molecular weight of polycarboxylate ether and C-S-H Jennite, it was determined that 1 molecule of polycarboxylate ether embedded in 155 C-S-H Jennite molecules resulted in 1.5% of the Polycarboxylate ether by weight in the cement composite mixture. Appropriate molecular modeling configurations were created for the MD analysis. Fig. 3 presents the molecular structure of polycarboxylate ether and C-S-H Jennite – Polycarboxylate ether composite molecular structure.

IV. RESULTS AND DISCUSSIONS

The predictive mechanical properties from MD analysis of C-S-H Jennite and Polycarboxylate ether composite structure is presented in Table II.

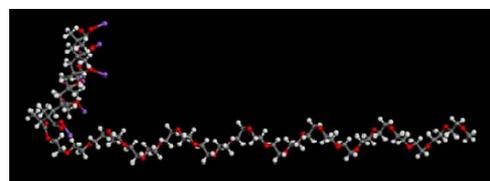
TABLE II
INFLUENCE OF PLASTICIZER ON THE MECHANICAL PROPERTIES OF C-S-H JENNITE (MD PREDICTIONS)

Material System	Mechanical Property			
	E (GPa)	ν	K (GPa)	G (GPa)
	Elastic modulus	Poisson Ratio	Bulk modulus	Shear modulus
Jennite	54.02	0.34	70.30	19.69
Jennite-Plasticizer	53.35	0.33	65.61	19.56

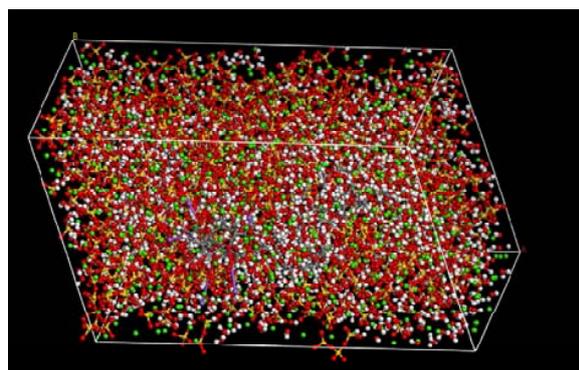
Clearly, MD simulations are effective to understand the predictive influence of nano additives to cement composite structures such as the one discussed in the present paper.

V. CONCLUDING REMARKS

Complex composite material systems such as cement paste where the properties are influenced by the material chemistry changes and additives require effective modeling methods to understand their predictive influence on their mechanical properties for cyber enabled material modeling. In this paper, mechanical properties of C-S-H gel using molecular dynamics and studied feasibility of MD modeling to understand the effect of addition of plasticizer in C-S-H. Overall, the results compared well with the other MD simulations and experimental values reported in the literature. Clearly, MD simulation analysis provided an upper bound value for these predicted mechanical properties and demonstrates the “scale effect” noticed in the material systems. Literature studies indicate that the material properties at the nano/molecular scale are higher than the values seen at higher length scales, including micron scale that could be attributed to the averaged values from higher scales than MD.



(a)



(b)

Fig. 3 (a) Polycarboxylate ether; (b) C-S-H Jennite and Polycarboxylate ether composite structure

ACKNOWLEDGMENT

The authors acknowledge the support by the U. S. Army Research Office under a cooperative agreement award contract no. W911NF-11-2-0043.

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