



## Molecular mechanisms of tricalcium aluminate under tensile loads

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### ARTICLE INFO

#### Keywords:

Molecular dynamics  
Interface Force field  
Uniaxial tension  
Puckered chain evolution  
Plane evolution

### ABSTRACT

A molecular dynamic study of the structure-property relationship of tricalcium aluminate subjected to uniaxial tensile loading has been investigated in this study. The suitability of interface force potential, being used in this study, has been verified against experimental observations and first principle calculations. The study demonstrates that energy associated with the non-bonded terms (Van der Waals, Coulombic and long-range interactions) contributes to the major part of the total energy which increases steadily with strain. Nucleation of voids are also observed in the post-peak regime. Different bond lengths and angles of the puckered chain, which constitute the crystal structure of the ionic-covalent solid, are observed to increase (either uniformly or non-uniformly) with application of load in the prepeak regime. It can also be observed that even though coplanarity of the O and Al atoms in the puckered chain is separately maintained throughout the straining process; the angle between the two different planes in the puckered chain are observed to increase with strain. For the first time in literature, this study provides details of the deformation mechanism at a molecular level of this ionic-covalent solid when subjected to uniaxial tensile loading situations.

### 1. Introduction

Tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ) is one of the major components in Mineral Trioxide Aggregate (MTA) and Partially stabilised cement (PSC) compounds that are used for dental root-end filling material and vital pulp therapy [1,2]. This material is also a component of the cement clinker for ordinary Portland cements [3] and is generally abbreviated as  $\text{C}_3\text{A}$  (where C represents  $\text{CaO}$  and A represents  $\text{Al}_2\text{O}_3$ ). It is well known that increasing the content of this material results in faster setting time at the expense of increasing the heat of hydration.

In Portland cement typically the setting time is around 4 h in which rate of reaction is controlled by calcium sulphate (gypsum) which is added by the manufacturer. The calcium sulphate reacts with the tricalcium aluminate in Portland cement to produce a high-sulphate calcium sulpho-aluminate (ettringite). The main consideration of cement industry is in strength. If the material reacts fast producing flash-set and increases heat of hydration, it might affect the mechanical performance of the final product. There has been numerous works in the cement industry in which researchers have tried to investigate the role of ettringite on mechanical performance at various levels [4–6]. However, the concern in dental industry is not much on strength but much more on rapid setting along with other factors like biocompatibility, non toxicity to pulp tissue, antibacterial properties and so on. Since the

amount of material used for dental activity is very small, the issue related to high heat of hydration is not a problem and in fact the rapid setting characteristic of the material is a blessing in disguise. It should also be realized that in absence of gypsum, tricalcium aluminate forms a hydrated calcium aluminate of cubic structure instead of ettringite.

In cement industry it is well known that  $\text{C}_3\text{A}$  constitutes around 5–15% of the cement clinker and upon hydration contains around 1–5% of unreacted material. The amount of  $\text{C}_3\text{A}$  in MTA or PSC is much more (molar ratios of tricalcium silicate to tricalcium aluminate is around 9/1, 7/3 and 5/5 – refer [2]) and thereby it can be anticipated that the hydrated material will also have a large amount of unreacted  $\text{C}_3\text{A}$  material. Given this situation, there is a need to study the molecular mechanisms of the material subjected to different loading situations. Out of different types of loading situations, tensile loading is being investigated in this study as it is being anticipated that there will be situations in which dental root filling material will be subjected to tensile loads. Moreover it should also be realized that the tension force primarily causes voids which eventually results in formation of cracks and eventual failure of brittle materials. Tensile loading has also been chosen in this study since it is well established that calcium silicate hydrates (hydrated products of tricalcium and dicalcium silicate) influence the compressive strength of the final product but there are no literature which have yet been able to explain the tensile response of

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<https://doi.org/10.1016/j.commsatsci.2018.08.058>

Received 27 June 2018; Received in revised form 26 August 2018; Accepted 27 August 2018

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the hydrated material.

Typically  $C_3A$  material can have  $\sim 0$ –2% of impurity in which  $Al^{3+}$  is replaced by  $Fe^{3+}$  and  $Si^{4+}$  whereas  $Ca^{2+}$  is replaced by  $Na^+$ ,  $K^+$  and  $Mg^{2+}$ . However, it should be noted that an impurity content more than 3% can result in rendering the crystal structure of the compound from cubic to orthorhombic and other polymorphs [3,7,8]. In this molecular mechanistic study we have considered the pristine cubic form of  $C_3A$ , as per literature review [9].

Apart from providing details about the crystal structure of the material [9], the existing literature determines the elastic properties of the crystal either through nano-indentation technique of synthetic materials [10] or through first principle calculations [11,12]. There exists only one study in literature which determines the elastic properties of  $C_3A$  at high pressure both experimentally as well as from first-principle calculations [11]. However, it should be noted apart from X-ray diffraction analysis and estimation of the lattice parameter along with the elastic constants at different pressures, the above mentioned literature does not delve into the intricacies of evolution of different bonds, angle and puckered chains on application of load; which is being demonstrated in this study.

Typically, any molecular dynamic study is dependent upon the force potentials being used for simulation. It should also be realized that given existing status of computers, it is also not feasible to run first principle calculation of these crystal structures with more unit cells under different loading situations. Thereby, a well calibrated (generally against first principle calculations and experimental validation) force potential should be chosen for study of the dynamics of the crystal structure under different loading situations. A well suited force potential, INTERFACE force field has been developed for  $C_3A$  [13] and its applicability against the determination of several physical and chemical properties has also been discussed extensively. It should be noted that INTERFACE force field has been developed recently [14] and it is currently a recognized force field for modeling of different constituents of cement and its hydrates [15] as well as various other different materials.

Since the behavior of the material is intrinsically related to the deformation evolution of the crystal lattice structure, the study under each set of conditions becomes important. Uniaxial tensile loading has been considered for this study. In a uniaxial tensile stress condition, the material is loaded in one direction and no restraints are placed on the other two transverse directions; thereby the material can experience both changes in the volumetric and deviatoric response. This type of loading and boundary condition is quite typical for pseudo static loading conditions in an universal testing machine and/or in a split-Hopkinson type experiments [16–18].

## 2. Simulation methodology

Reported and widely accepted structure of  $C_3A$  at ambient temperature and pressure condition [9] is a cubic crystal ( $a = b = c = 15.263 \text{ \AA}$  and  $\alpha = \beta = \gamma = 90^\circ$ ) belonging to space group  $Pa\bar{3}$ . One unit cell of  $C_3A$  consists of 72 Ca, 48 Al and 144 O atoms where Al and O atoms are covalently bonded and Ca atoms are present as ions. Six Al atoms and eighteen O atoms together form  $Al_6O_{18}$  puckered ring structure (Fig. 1b) and there are eight such puckered rings in a unit cell (Fig. 1a). There are two types of O atoms in the puckered ring named as  $O^{ring}$  and  $O^{apical}$ , where  $O^{ring}$  atoms are part of the ring itself and  $O^{apical}$  atoms are connected to the Al atoms of the ring. All Al and  $O^{ring}$  atoms of the ring do not lie in the same plane. Alternative  $O^{ring}$  atoms (1,5,9 and 3,7,11) as well as Al atoms (2,6,10 and 4,8,12) (Fig. 1b) are in different planes in the reported structure [9]. In this study 5 such unit cells in each three directions ( $5 \times 5 \times 5$ ) have been used to construct the simulation box (box dimension:  $lx = ly = lz = 76.315 \text{ \AA}$ ). Total numbers of atoms in the simulation cell is 33000 (9000 Ca, 6000 Al and 18000 O atoms). There are 1000 puckered rings in the simulation box.

INTERFACE force field [14] (which has been parameterized to efficiently reproduce the experimental results for structural properties – cell parameters, surface/interface properties, mechanical properties and vibration spectra) is adopted for the study. The harmonic energy expression of PCFF force field (Ref. Eq. (1)) has been adopted corresponding to the INTERFACE parameters. It consists of quadratic bond and angle interaction, as well as coulombic and 9-6 Lennard-Jones nonbonded interactions where  $K_0$ ,  $r_0$ ,  $K_\theta$ ,  $\theta_0$ ,  $\epsilon$ ,  $\sigma$  are the parameters representing vibrational constants for bond stretching, equilibrium bond length, vibrational constants for angle bending, equilibrium bond angle, equilibrium non-bonded energy and equilibrium non-bonded distance of same type of atoms respectively. Sixth power combination rule is used to compute the non-bonded coefficients for different type of atoms interacting with each other. It is to be noted that atoms under bond and angle interactions are excluded (1,3 nonbond scaling) during the calculation of the non-bonded interactions.

$$E_{pot} = \sum_{\substack{ij \\ \text{bonded}}} K_{r,ij} (r_{ij} - r_{0,ij})^2 + \sum_{\substack{ijk \\ \text{bonded}}} K_{\theta,ijk} (\theta_{ijk} - \theta_{0,ijk})^2 + \frac{1}{4\pi\epsilon_0} \sum_{\substack{ij \\ \text{nonbonded} \\ (1, 3 \text{ excluded})}} \frac{q_i q_j}{r_{ij}} + \sum_{\substack{ij \\ \text{nonbonded} \\ (1, 3 \text{ excluded})}} \epsilon_{ij} \left[ 2 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^9 - 3 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

The sum of Van der Waals interaction, electrostatic (Coulombic) and long range interaction constitute the non-bonded energy part. The coulombic part primarily considers the interaction of Ca ion with other atoms as well as with itself. In this regards it is to be mentioned that Al and O atoms which are separated by three consecutive bonds (1,3 non-bond scaling) also take part in non-bonded interaction which indirectly contributes to the ionic-covalent nature of Al-O bonds.

Molecular Dynamic simulation is performed using large scale massively parallel simulator (LAMMPS) [19] package. The potential energy minimized simulation box is equilibrated under isobaric-isothermal (NPT) ensemble at ambient pressure (1 atm) and temperature (298 K) for 100 ps with time step of 0.2 fs. Nose/Hoover thermostat and barostat have been used for this simulation. Convergence of pressure, temperature and total energy are ensured within the simulation time of 100 ps. The final equilibrated simulated structure ( $lx = ly = lz = 76.272$  i.e.  $a = b = c = 15.254 \text{ \AA}$ ) gives good correlation with the experimental results with an error margin less than 0.1% for lattice parameters. The mean  $Al-O^{ring}$  bond length is  $1.747 \text{ \AA}$  which is smaller than the experimental value of  $1.755 \text{ \AA}$ ; whereas the mean  $Al-O^{apical}$  bond length is  $1.749 \text{ \AA}$  which is close to the experimental value of  $1.750 \text{ \AA}$ . Bond angle  $O^{ring}-Al-O^{ring}$ ,  $O^{ring}-Al-O^{apical}$ ,  $O^{apical}-Al-O^{apical}$ ,  $Al-O^{ring}-Al$  are computed as  $113.3^\circ$ ,  $105.5^\circ$ ,  $123.2^\circ$ ,  $151.3^\circ$  respectively whereas the corresponding experimental values are  $111.8^\circ$ ,  $105.4^\circ$ ,  $123.1^\circ$  and  $152.3^\circ$ . From observations it can be mentioned that the used force field is quite accurate for simulation of structural parameters under different loading situation.

Periodic boundary condition (PBC) have been used for simulation of applied loading conditions. Non-bonded cut-off length has been taken as  $10 \text{ \AA}$  and particle-particle particle-mesh (PPPM) solver [20] with convergence criterion of  $10^{-6}$  is adopted for long-range electrostatics interactions.

To simulate the uniaxial stress condition, the system is elongated at a constant strain in one axial direction while the other two perpendicular direction are subjected to NPT condition with zero target pressure. This condition enables the transverse directions to relax freely without having any stress and pressure evolution in those directions. The simulation box is elongated up to a strain of 0.3 to capture the yield

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