

# Modeling of glycidoxypropyltrimethoxy silane compositions using molecular dynamics simulations



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## ABSTRACT

Glass fibers in glass-epoxy composites typically require a coating, called the sizing layer, which facilitates manufacturing and contributes to the overall mechanical properties. In this work, the structure and mechanical properties of a common sizing material, glycidoxypropyltrimethoxy silane (GPS), are studied using reactive all-atom molecular dynamics (MD) simulations. In the sizing layer, a network structure forms by inter-GPS connections through Si—O—Si linkages. Silicon atoms of the GPS molecules can participate in zero, one, two or three Si—O—Si linkages, and create T0, T1, T2 and T3 species, respectively. Sizing layer models consisting of 100% GPS are prepared with several different compositions of these species. Properties of the structure (i.e., density, radial distribution function, and interstitial space), mechanical properties (modulus, strength, strain and energy absorption), and failure modes of the sizing layer are studied. Simulation results indicate that mechanical properties of the sizing layer could be tailored by changing the species compositions.

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## 1. Introduction

Sizing is a thin coating applied to the glass fiber surface during the fiber manufacturing process that protects the fiber from handling damage and also controls the level of adhesion between the fiber and matrix [1]. It is an important component involved in the manufacturing of glass fibers and their composites. Most of the glass fiber sizing contain silane-based coupling agents, along with other components like film former (FF), surfactant, and lubricant [1–8]. The silane chemistry is chosen to tailor the level of reactivity with the fiber surface, and the polymer matrix such as an epoxy. In the sizing layer, silane forms a cross-linked network through Si—O—Si linkages [8]. The sizing layer is also coupled to the glass surface through Si—O—Si linkages. Silicon atoms of the silane molecules can participate in zero, one, two or three Si—O—Si linkages, giving rise to T0, T1, T2 and T3 species, respectively, as shown in Fig. 1. Depending on the processing conditions

(especially temperature, pH level and time), the number density of these species and the morphology of the network structure vary, which is expected to influence the properties of the interphase that develops during composite processing. For example, when the glass fibers with sizing are enveloped by an amine-cured epoxy thermoset matrix during the composite processing, interdiffusion of the film former, surfactant, resin and curing agent molecules occurs due to concentration differences. During this diffusion process, the silane and resins undergo an epoxide-amine reaction, leading to the formation of an interphase region. The atomic structure of the sizing network that exists prior to interphase formation is expected to have a significant influence on the interphase properties in the composite.

Some previous experimental studies have focused on the chemical kinetics of the formation of silane-based sizing structures and how the sizing based interphase affects overall composites properties [4,8–10]. de Buyl et al. [8] studied the reaction kinetics (hydrolysis and condensation reactions) of sizing network structure formation in aqueous solution at constant pH level, where they found that the kinetics are dramatically accelerated at elevated temperature (50–70 °C). Pavlovic et al. [9] likewise found

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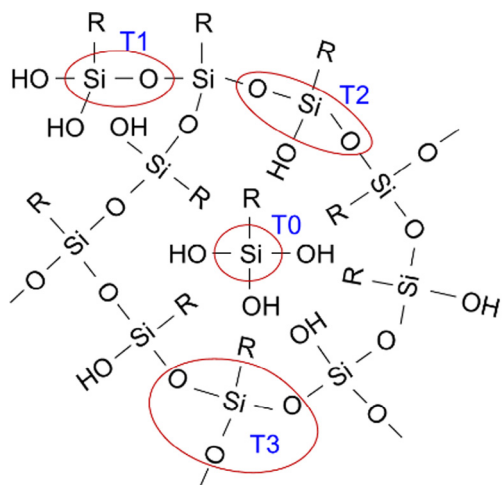


Fig. 1. Schematic of silane network with T0, T1, T2 and T3 species.

that higher curing temperatures promotes the creation of more siloxane bonds (i.e., Si–O–Si linkages), resulting in a highly cross-linked network. However, to the best of our knowledge, a systematic study of the relationship between the properties and the molecular-scale structure of the sizing layer has not yet been reported in the literature. Here, we conduct a systematic study using molecular simulations to determine the structure and mechanical properties of different silane composites comprised of T0, T1, T2 and T3 species used in glass/epoxy sizing as a first step towards interphase design using computational methods.

In this paper, the properties of sizing layers based on glycidoxypropyltrimethoxy silane (GPS), a common sizing component, are studied using all-atom molecular dynamics (MD). We consider six different combinations of T0, T1, T2 and T3 species, i.e., T0:T1:T2:T3 = 00:00:00:100, 00:00:100:00, 00:00:50:50, 00:00:75:25, 10:10:40:40 and 25:25:25:25. The structure, mechanical properties, and failure modes are studied. MD simulations are conducted using LAMMPS [11]. Atomic interactions are modeled by the non-reactive general AMBER force field (GAFF) [12] during the network structure development, and by the reactive force field ReaxFF [13] during the mechanical deformation to incorporate nucleation and growth of damage resulting from bond scission.

## 2. Model development and simulation details

In an experimental study, de Buyl et al. [8] reported that the GPS network structure had  $T1 + T2 > 80\%$ ,  $T0 \sim 10\%$ , and  $T1 < 10\%$  in 2.0 wt% GPS aqueous solution at pH level  $\sim 5.4$  and room temperature. In commercial glass fiber sizing solutions, the GPS concentration ranges from 0.05 to 3.0 wt%. Likewise, the temperature, pH, and processing time can vary substantially, potentially creating a wide spectrum of network compositions. Therefore, to study the effects of network composition on mechanical properties of the sizing layer, six models with T0:T1:T2:T3 = 00:00:00:100, 00:00:100:00, 00:00:50:50, 00:00:75:25, 10:10:40:40 and 25:25:25:25 are created. For convenience, these models are designated from Model-1 to Model-6. To improve sampling of conformational space and obtain a statistical average, three independently constructed replica structures of each composition are considered.

The model development scheme can be divided into two stages. In the 1st stage, sizing network structures are prepared using a single-step cross-linking algorithm. Details of the algorithm can

be found elsewhere [14,15]. In this stage, all the intra- and intermolecular interactions have been modeled by the general AMBER force field [12]. The reactive force field ReaxFF [13] is used during the mechanical deformation to capture bond breaking. ReaxFF has a significantly different functional form and parameter set than AMBER, including a continuous bond distance/bond order relationship and a polarizable, geometry-dependent charge calculation – enabling ReaxFF to simulate bond-breaking and formation processes [13]. Changes in the force field might induce internal stresses, deviating from the equilibrium state of the model. In the 2nd stage, the developed models have been equilibrated with ReaxFF to reduce the internal stress. The equilibration protocol is presented in the next section. A full description of all ReaxFF potential functions can be found elsewhere [16]. The ReaxFF parameter used in this study was generated by merging and re-training compatible versions for water/alkane [17], protein [18] and oxides [19] together so that it could describe the energies and forces of all combinations of atomic interactions present in the sizing materials. We used this parameter set to model silica-silane interaction [20]. This parameter set is also capable of modeling epoxide-amine interaction in polymer.

### 2.1. Sizing layer model development

#### 2.1.1. Stage – 1

To create the sizing network structure, a three-dimensional cubic box is randomly filled with hydroxylated GPS molecules (Fig. 2a). The mixture is hydrostatically compressed at 700 K temperature and 100 atm pressure in the NPT ensemble to rapidly equilibrate the density. The mixture is further equilibrated at 700 K temperature and 1 atm pressure with NPT ensemble. Then the cross-linked structure with specific combinations of T0, T1, T2 and T3 species is created using the cross-linking algorithm. Cross-linked structures are formed through condensation reaction between the hydroxyl groups of the adjacent GPS molecules (Fig. 2b). This equilibration and cross-linking procedure produces a reasonable network structure, and the network properties are not particularly sensitive to the precise small-scale network structure, as shown in previous studies [21,22].

#### 2.1.2. Stage – 2

The network structure developed in stage – 1 is then equilibrated with the ReaxFF force field with the following steps: (i) heat the system gradually by increasing temperature from 1 K to 300 K for 500 ps (picoseconds) with NPT ensemble at 1 atm pressure; and (ii) NPT equilibration at 300 K temperature and 1 atm pressure for 750 ps. Fig. 3 shows a representative replica of Model-1.

### 2.2. Mechanical loading and boundary conditions

To determine the mechanical properties, the models have been subjected to uniform uniaxial tensile strain in each of the three orthogonal directions (i.e., X-, Y-, and Z-direction) independently. Strain is applied in the three orthogonal directions to have the average mechanical properties. Uniaxial tensile strain of the solution domain is achieved by linearly expanding the coordinates of all atoms along the specific direction at every time step with a constant strain/displacement rate (i.e., affine deformation) [23,24] followed by MD time integration. To mimic the plane-stress condition, transverse direction movements due to Poisson's effect are allowed (i.e. zero force in these directions). A time step of 0.2 fs (femtoseconds) is used and NPT ensemble at 300 K and 1 atm pressure is considered. The strain rate used in the mechanical loading is  $5.0 \times 10^9$ /s.

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