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Material properties of the cross-linked epoxy resin compound predicted by molecular dynamics simulation

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Abstract

Molecular dynamics (MD) simulations were conducted to estimate the material properties of the cross-linked epoxy resin compound. A periodic amorphous structure of the cross-linked epoxy resin compound was constructed and it was simulated by continuous accumulation of structure configurations at various temperatures. Based on the simulation results, glass transition temperature (T_g), linear thermal expansion coefficients and Young's modulus of the cross-linked epoxy resin compound were predicted. The predicted values of these material properties are in good agreement with the experimental values in the literature.
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Keywords: Molecular dynamics simulation; Cross-linked epoxy resin; Material properties

1. Introduction

With the increasing need for high input/output (I/O) counts and miniaturization, novel electronic packages are continuously being developed. Wafer level packaging technology is becoming popular due to low cost and higher electronic performance. Epoxy resin is widely used in electronic packaging and its performance is very important to the reliability of electronic packages. To obtain good performance of these materials and guide the experimental research, it is important to understand the material properties of epoxy materials, such as Young's modulus, T_g and coefficients of thermal expansion at a fundamental level. Moreover, as the feature size shrinks and the interfacial material characterization becomes a more dominant factor in the package performance, investigations at the molecular level are becoming important and necessary.

Molecular modeling is the science of representing molecular structures numerically and simulating their behavior with the equations of quantum and classical physics and it is one of the fastest growing fields in science. The molecular dynamics (MD) method was first introduced by Alder and Wainwright in the late 1950s to study the interactions of hard spheres [1,2]. The method is now a well-established and important tool that endeavors to simulate the material measurement on an atomistic scale in order to understand the basic origins of material performance. Electronic effects are averaged out in MD method, the process of a chemical reaction involving bond-forming, bond-breaking and charge transfer cannot be described using MD simulation. However, it can be used to describe the performance of large and complex organic, inorganic and solid state systems due to its cheap and fast calculation. Molecular dynamics (MD) simulations have been successfully applied to predict material properties throughout the last decade. Hamerton et al. [3] used MD simulation to calculate physical and mechanical properties of polyarylethersulfones and showed that modeling of polymers in the bulk gave insights into the factors governing the observed physical and mechanical properties. MD simulation was performed to examine the glass transition temperature (T_g) in poly(methyl methacrylate) at different length scales and in different time range by Tsige and Taylor [4]. MD

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simulations were carried out to examine T_g of the freeze-dried formulation containing polymer excipients by Yoshioka et al. [5], and they presented that MD simulation was a useful method for investigating the effect of hydration and molecular weight on the T_g of the freeze-dried formulation containing polymer excipients. Yang et al. [6] performed MD simulations of the glass transition through isobaric and isochoric cooling of a model polymeric material and excellent agreement between the simulation results and the existing experimental trends was observed. Sorption induced glass transition in an amorphous polyethylene like polymer was investigated by Van et al. [7] using molecular dynamic simulations. Qi et al. [8] used MD simulations to investigate material properties of an aromatic polyimide and its mixture with carbon nano tube. Most of these studies have been focused on thermoplastic materials, such as poly(methyl methacrylate), polyethylene, and polyarylethersulfones. However, due to the complexity of the cross-linking reactions, little attention was paid to the material properties of the thermoset materials, especially the cross-linked epoxy resin compounds widely used in electronic packaging. Its performance is very important to the reliability of electronic packages. Prediction and better understanding of its properties would be necessary and significant on the design and development of the cross-linked epoxy resin compounds in electronic packaging.

MD models of the cross-linked epoxy resin compounds were ever investigated by some researchers. Yarovsky and Evans [9] investigated the strength and molecular mechanisms of adhesion between an inorganic substrate and a cured epoxy resin using MD simulation. They presented a method to predict cross-link density in the physical mix of the resin and curing agent molecules. However, there are lots of issues on the identification of the reactive sites and covalent bonds formed between the resin and curing agent molecules. Gou et al. [10] used MD simulations to predict the interfacial shear strength based on a cured epoxy resin model, which was constructed by incorporating fully cross-linked network of macromolecules formed during curing reaction. Mijovic and Zhang [11] also conducted MD simulation to investigate the interactions and dynamics of water in a fully cured epoxy–amine network. Both MD models of epoxy resin compounds were described as a fragment of fully cured network consisting of several molecules of epoxy resin and curing agent. Based on their MD models, the fundamental knowledge obtained from MD simulation together with the experimental measurement was used to develop a methodology for the better prediction of the material properties.

In this study, molecular dynamics (MD) simulations were carried out to predict the material properties of the fully cured epoxy network composed of EPON 862 epoxy resin and TETA–triethylenetetramine curing agent. T_g was estimated based on the discontinuity in the slope of the density–temperature plot from MD simulations. The linear thermal expansion coefficient and Young's modulus of the cross-linked epoxy resin were also obtained from MD simulations. The predicted material properties from MD simulations are much close to the experimental values in the literature.

2. Molecular dynamic simulation

MD simulations were conducted using Materials Studio (Accelrys Inc.) software. The polymer consistent force field (PCFF) was used in this simulation. The PCFF for polymers and other materials is intended for application to polymers and organic materials. It is useful for polycarbonates, melamine resins, polysaccharides, other polymers, organic and inorganic materials, about 20 metals, as well as for carbohydrates, lipids, and nucleic acids. PCFF can also be used to calculate cohesive energies, mechanical properties, compressibility, heat capacities, and elastic constants. The Velocity Verlet algorithm was used for integration in all the MD simulations. The non-bond interactions with a cutoff distance of 9.5 Å include van der Waals and electronic static forces. The Ewald approach was used for the dispersion interactions. In this study, MD simulations were performed on the fully cured epoxy resin compound.

The fully cured epoxy network is composed of EPON 862 resin and TETA–triethylenetetramine curing agent. During the curing reaction, the hydrogen atoms in the amine groups of curing agent molecules reacted with the epoxide groups of epoxy resins. Initially, one epoxide group reacted with one curing agent molecule. The resulting molecule can further react with other epoxy molecules at the site of NH and NH_2 and one curing agent molecule at the site of another epoxide group (Fig. 1). As the reaction continues, more cross-links are generated by the epoxy resin and curing agent molecules. The cross-linking activity expands in all directions and forms a network of macromolecules.

In the literature [12], the thermal properties of the compound were measured using standard thermal mechanical analyzer (TMA). The mixed epoxy resin and curing agent compound were initially cured for 24 h at room temperature, and subjected to post cure for 2 h at 121 °C. TMA experiment started at 25 °C under a pressure of 0.1 MPa and temperature was heated to 20 °C above T_g at a rate of 5 °C/min. T_g and thermal expansion coefficients, respectively, were obtained from the temperature at the break in the volume change curve and the slop of the volume change curve.

Based on the weight ratio (100:15.4) of the mixed epoxy and the curing agent in the literature [12], a fragment of fully cured network consisting of 12 molecules of EPON 862 epoxy resin and 4 molecules of TETA was built and an amorphous structure was constructed using amorphous builder in Materials Studio software. Totally 628 atoms were assembled in a cubic cell with a density equal to the experimental value of 1.23 g/cm^3. To avoid surface effect, periodic boundary conditions in all directions were used. The amorphous structure was then subjected to an energy minimization at room temperature using the ensemble of the constant volume and temperature (NVT).

In order to investigate the effect of the cell size on the simulation results, three kinds of MD models with the same density at room temperature were built. The fragment of fully cured network in three models consisted of different amounts of EPON 862 epoxy resin molecules and TETA molecules,

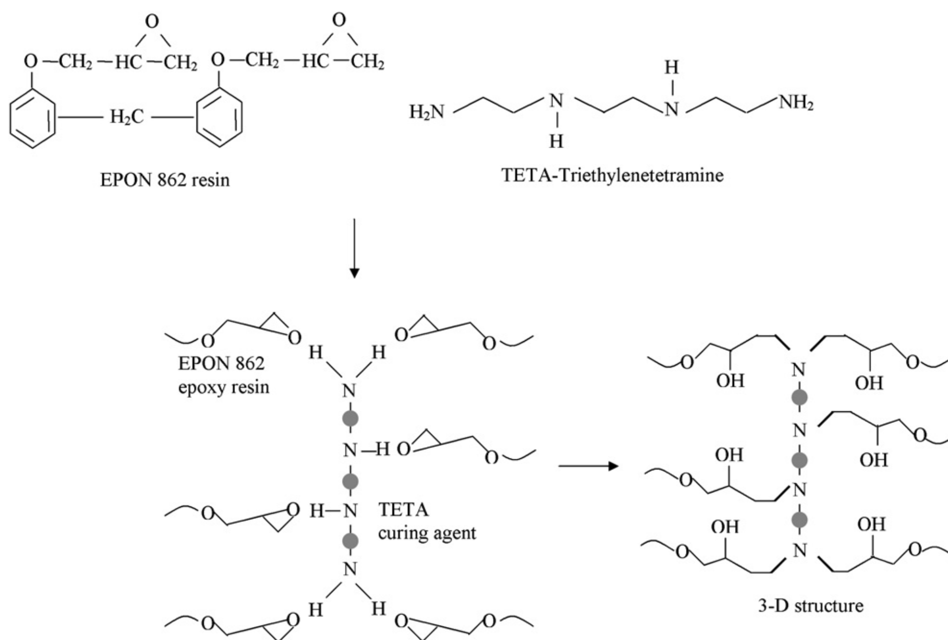

Fig. 1. Reaction of a curing agent with four epoxy resins.

which is listed in Table 1. All the models were conducted at both 25 and 125 °C for 200 ps using the ensembles of the constant number of particles, constant-pressure and constant temperature (NPT). The calculated volume for each kind of model is listed in Table 1. It was found that the calculated volume was nearly proportional to the amount of the epoxy resin and TETA molecules. It means that the cell size has no large effect on the calculated properties. Therefore, to reduce the computational requirement, the smallest size of cell was used in the following simulation. The effect of simulation time on the simulation results was also investigated and the results indicated that the simulation time in this study was sufficient for the convergence of simulation results.

In order to imitate the thermal performance in a kinetic process, MD simulation of a cooling process was performed. MD simulations were conducted starting at 225 °C under a pressure of 0.1 MPa using NPT ensembles. Temperature was cooled to room temperature at a rate of 10 °C/200 ps, which was controlled by the nose method. Each subsequent simulation was started from the final configuration obtained at the preceding temperature. The simulation in each case study was performed with an interval of 1 femtosecond (fs) in each MD simulation step.

Table 1
Calculated volume for the MD models with different cell sizes

Number of epoxy resin	Number of TETA	Volume[a] (nm^3)	Volume[b] (nm^3)
12	4	40.62	41.64
18	6	60.27	63.20
24	8	82.45	82.15

[a] 25 °C.
[b] 125 °C.

3. Results and discussion

Density of the cured epoxy at each temperature was calculated from the average specific volume of the system, as shown in Fig. 2. A steady increase of the density with decreasing temperature and a clear change in the slope of the density curve were observed. The change in the slope of the density curve defines the value of the glass transition temperature (T_g), at approximately 109 °C, where the epoxy resin passes from a glassy state to a rubbery state. It was observed that the assigned cooling rate affects the predicted value from MD simulations [5,6]. The mobility of the polymer chains rapidly decreases when the polymer melt is cooled below T_g, and sufficient long time is needed for the equilibrium structure. Higher cooling rate in the simulation can increase the departure from the equilibrium state, which results in higher value

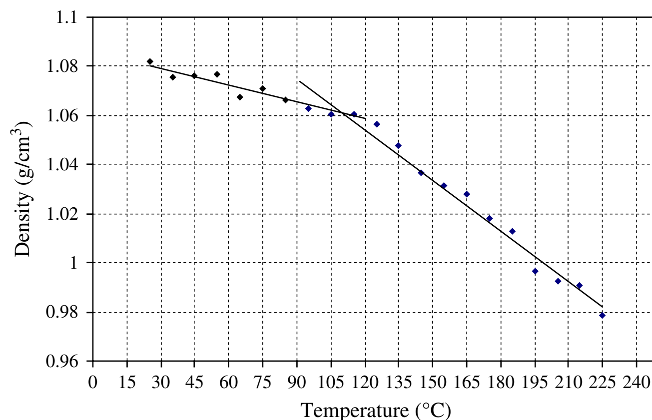

Fig. 2. A plot of the density as a function of temperature.

Table 2
Material properties from both MD simulation and experimental data in Ref. [12]

Material properties	Ref. [12]	MD simulation
Young's modulus (GPa)	3.43	3.75
T_g (°C)	105	109
β_1 (below T_g) (ppm/°C)	61.0	55.3
β_2 (above T_g) (ppm/°C)	195.0	184.7

of T_g from MD simulations. The cooling rate chosen in present study was fined-tuned so that the predicted value of T_g from molecular dynamic simulation is expected to be very close to the experimental value from the literature [12] listed in Table 2.

The initial volume of the system from MD simulations was 36.20 nm^3 and the corresponding volume of the system at each temperature from MD simulations was obtained. The volume thermal expansion coefficient, α, is defined by the following equation:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{1}$$

where T is the temperature, P is the pressure, and V is the volume.

The change in the volume of the cell structure against the temperature is given in Fig. 3. At both high and low temperatures, the volume change decreased linearly with the decreasing temperature. The abrupt change in the curve also defined the glass transition temperature. The data at temperature above and below T_g were fitted using the linear regression, $y = ax + b$, respectively. The volumetric thermal expansion coefficients for both the glassy and rubbery state were obtained from the two slopes of the curve which discontinues at the glass transition temperature. For isotropic materials, the linear thermal expansion coefficient, β , is related to the volumetric thermal expansion coefficient by

$$\beta = \frac{1}{3}\alpha \tag{2}$$

The linear thermal expansion coefficients for both the glassy and rubbery state were calculated and are listed in Table 2.

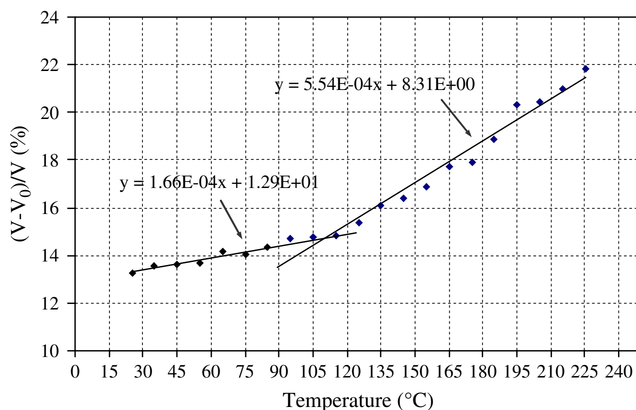

Fig. 3. Volume change against temperature and the two fitted straight lines.

The equivalent-continuum constitutive equation was used to describe the mechanical behavior of system with the discrete structure at an atomic scale. The constitutive equation of the equivalent continuum is given as follows:

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl} \tag{3}$$

where σ_{ij} are the components of stress tensor. In an atomistic calculation, the internal stress tensor in a system was obtained using the so-called virial expression as follows [13]:

$$\sigma = -\frac{1}{V_0}\left[\left(\sum_{i=1}^{N} m_i\left(v_i v_i^T\right)\right) + \left(\sum_{i<j} r_{ij} f_{ij}^T\right)\right] \tag{4}$$

where i is the particle number, m_i, v_i and f_i are the mass, velocity of the particle and force acting on the particle, respectively, and V_0 is the volume of the system.

The strain tensor, the expression of the change of the relative position of the particles resulted from the stress, can be given as follows [13]:

$$\varepsilon = \frac{1}{2}\left[\left(h_0^T\right)^{-1} G h_0^{-1} - 1\right] \tag{5}$$

where h_0 is the matrix of the initial dimension of the structure, h is the matrix of the dimension of the deformed structure, and G is the metric tensor $h^T h$.

Based on the stress–strain relation, the elastic stiffness coefficients can be obtained. For the isotropic material, the stress–strain behavior can be described by only two independent coefficients, Lame coefficients, λ and μ, which are same as that described at a macro-scale level. Therefore, the mechanical properties of material from MD simulation, such as Young's modulus, can be given as follows [13]:

$$E = \mu\left(\frac{3\lambda + 2\mu}{\lambda + \mu}\right) \tag{6}$$

From the above equations, Young's modulus of the fully cured epoxy resin compound was also calculated from the MD simulations and is listed in Table 2.

The predicted values of both coefficient of thermal expansion and coefficient of Young's modulus from the MD simulations are very close to the experimental values from the literature [12] with a small variation within 10%. The small difference between the MD simulation and experimental values can be attributed to the lower cross-link density of the epoxy resin compound in the experimental results from the literature [12]. In reality, it is most likely that a certain amount of components (EPON 862 and TETA) are not fully cross-linked in the epoxy resin compound, which allows the sample to produce larger strain than the idealized situation stipulated in the MD simulation modeling a fully cross-linked network. Therefore, the epoxy resin compound is rather soft and bears large deformation, which results in lower modulus and higher thermal expansion coefficients. Moreover, voids or impurity inside the epoxy compound can also degrade these material properties.

The predicted material properties from MD simulations are in good agreement with the experimental values from the literature [12], which confirms the accuracy of the cured epoxy resin model, the properness of the force field and the cooling rate. Comparing to other researches [2–8], the present MD model attempted to predict material properties of the cured epoxy resin, which is of higher complexity of the structure. The predicted material properties of an epoxy resin compound prior to laboratory design can guide the design and development of a new epoxy resin compound with higher quality, which is widely used in electronic packaging.

4. Conclusions

In summary, the results have demonstrated the usefulness of the MD simulations as a tool to determine the material properties of the cross-linked epoxy resin compound. It is shown to provide an effective and accurate estimation of the material properties of epoxy resin compound at macro-scale. The cooling rate chosen in this study was fined-tuned so that the predicted value of T_g from molecular dynamic simulation was expected to be very close to the experimental value in the literature. Low cross-link density of the epoxy resin, voids and impurity inside the epoxy compound may result in the degraded material properties comparing with those from MD simulations. The results serve to confirm that MD simulation is getting to stage to find wide application in modeling epoxy resin application in various fields, particularly in electronic packaging.

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