Reactive and Functional Polymers 111 (2017) 60–67

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react

Mechanism of modulus improvement for epoxy resin matrices: A molecular dynamics simulation

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ARTICLE INFO

Article history:
Received 8 September 2016
Received in revised form 13 December 2016
Accepted 20 December 2016
Available online 21 December 2016

Keywords:
Molecular dynamics simulation
Epoxy resin
Structure–property relationship
Carbon nanotube
Curing agent

ABSTRACT

Theoretical modulus of three kinds of epoxy matrices, including diethylene toluene diamine (DETDA)/4,5-epoxyclyclohexyl-1,2-diglycidyldiformate(TDE85), *m*-phenylenediamine (MPD)/TDE85 and single-walled carbon nanotube (SWCNT) reinforced DETDA/TDE85 were investigated via molecular dynamics (MD) simulation to establish the structure–property relationships. The flexibility and mobility of molecular chains, the packing ability of cross-linked chain segment, the fraction of free volume of epoxy resins and the cohesive energy density in different epoxy systems were analyzed in detail, respectively. The MD simulation results showed that both the slight modification in the diamine structure and the introduction of SWCNTs can result in significant changes in the microstructure parameters of epoxy matrix, however, the modulus improvement mechanisms through changing curing agents and incorporating SWCNT into epoxy matrix had similarities and differences. The MD simulation method will be of great value in predicting and analyzing some performance closely related to the microstructure parameters for the different cross-linked resin system and its composite materials.

1. Introduction

Epoxy resin is one class of materials which are often used as polymer matrix in carbon fiber composites [1–3]. Epoxy resin matrices need to possess high modulus in some special applications, such as carbon fiber reinforced epoxy matrices composite vessels for high-pressure storage [4]. According to the existing reports, increasing Young's modulus of the epoxy resin matrices would improve the compression strength, transverse strength and interfacial shear strength of the carbon fiber reinforced composites [5,6]. High modulus of epoxy resin matrix can be obtained by using appropriate curing agents, and it also can be realized when some nanofillers are dispersed in the matrices [7–9]. However, it is a difficult task to select a proper curing agent from the wide variety of chemistry structures available and predict how it will perform under specific conditions because subtle difference in chemistry structure can produce drastic changes in external performance. Moreover, different size and shape of nanofillers (such as carbon nanotubes) also show varied effects on the mechanical properties of polymer matrices [10–12]. Experimental study on mechanical property of epoxy resins and nano-modified resin matrices will be time-consuming and inefficient duo to their multifarious chemical structures and complex cross-linked networks. The results showed that [13], even if carbon fibers were fully impregnated with epoxy resin, the resin matrix with a high modulus was found to be an essential prerequisite to excellent mechanical and interfacial properties of the resulting composites. Consequently, the ability to predict specific engineering properties, such as modulus of epoxy resin matrices according to material characteristics of curing agent and nanofillers is very important to the design and application of carbon fiber composites. Thus it is of great significance that understanding how the microscopic structure changes which are caused by choosing different curing agents and incorporating nanofillers into matrices affect the modulus of cured epoxy resins.

Molecular dynamics (MD) simulations which can cope with atomic details have been very successful in exploring various external characteristics and relating these characteristics to the molecular structure. Li et al. [14] studied the thermo-mechanical response of a thermosetting polymer composed of epoxy EPON 862 and curing agent DETDA by using MD simulation method. The relationships of the effect of crosslink density and thermomechanical properties of cross-linked epoxy resin have also been investigated by Bandyopadhyay et al. [15]. MD simulations also possess an inherent advantage in addressing nanoscale issues which are significant for performance analysis of nanocomposites. Gou et al. [16] studied the interfacial bonding of single-walled nanotube reinforced epoxy resins (EPON 862) through MD simulation. The glass transition and thermoelastic properties of cross-linked epoxy-based nanocomposites and their filler-size dependency were investigated

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http://dx.doi.org/10.1016/j.reactfunctpolym.2016.12.014
1381-5148/

with the help of MD simulation by Choi et al. [17]. Zhu et al. [18] simulated the stress–strain relations and the Young's moduli along the longitudinal direction. A. R. Alian et al. [19] conducted MD simulations to study the interfacial and the transversely isotropic mechanical properties of the nanoscale RVE containing CNT in epoxy. Thus, MD simulation is a feasible route for analyzing of experimental results and prediction of new material characteristics.

In this study, the mechanism of modulus improvement caused by varying chemical structures in the diamine curing agent and adding SWCNTs into epoxy matrices were investigated, respectively, by using atomistic modeling techniques. The structure–property relationships for the cured epoxy resins had been established by analyzing how the change of micro structure parameters arising from different chemical structure of diamine curing agent and the introduction of SWCNTs would affect the modulus of epoxy matrices.

2. Methodology

2.1. Simulation

To investigate the effect of chemical structure of diamine curing agents and the introduction of SWCNTs cells, Material Studio software v6.0 was used to construct models of different epoxy resin systems, including diethylene toluene diamine (DETDA)/4,5-epoxyclyclohexyl-1,2-diglycidyldiformate(TDE85), *m*-phenylenediamine (MPD)/TDE85 and single-walled carbon nanotube (SWCNT) reinforced DETDA/TDE85 systems were built and calculated. The armchair SWCNT (6, 6) with a diameter of 8.1 Å and aspect ratio of 3.02 were adopted in this work. The mass fraction of SWCNT was 2 wt.% embedded in the amine-epoxy matrix. The cell systems studied in this work consisted of 300 epoxy resin TDE85 molecules and 225 curing agent molecules (DETDA or MPD), respectively, which corresponded to approximately 15,900– 19,500 atoms in the simulation cell. The periodic boundary systems with parameters of 68 Å × 68 Å × 68 Å were used in this work. The epoxy resin, curing agents along with their cross-linking reaction are shown in Fig. 1. The cross-linking methodology and the modeling process followed the approach employed in the work [18,20]. The curing degree in cross-linked systems under current investigation was set to 80% and the configurations of the modeled unit cells are shown in Fig. 2.

All three resin systems were minimized using conjugate gradient method and then performed 5 annealing circle from 300 K to 500 K to release excessive energy of system. A further geometry optimization was conducted to acquire a conformation with the lowest energy. Thereafter, the dynamic simulation with constant volume (NVT) ensemble at 300 K for 500 ps, followed by a constant pressure (NPT) ensemble simulation at 300 K and 1 atm for 2 ns to obtain full equilibration of the temperature and density, respectively [17–18,20]. Once the initial equilibrated systems were achieved, a series of molecular dynamics simulations were performed at 300 K.

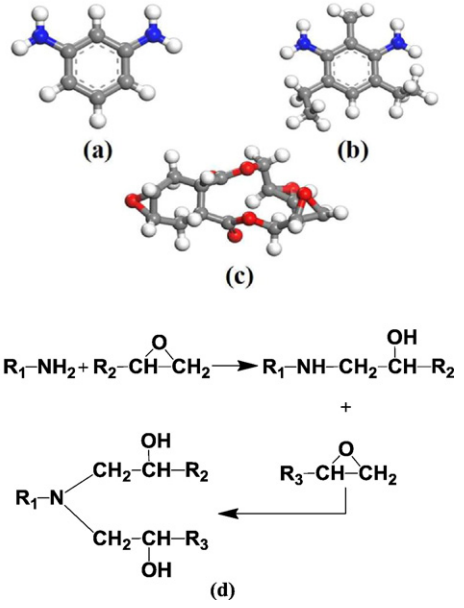

Fig. 1. Molecular structure of (a) MPD; (b) DETDA; (c) TDE85; (d) Crosslinking reaction; Atoms: gray (C), white (H), red (O), blue (N).

2.2. Experimental test

The epoxy resin TDE-85 (epoxy value, 0.85) was supplied by Tianjin Jindong Chemical Factory, China. DETDA (active hydrogen equivalent: 45; supplied by Lonza Chemicals Co., Switzerland) and MPD (active hydrogen equivalent: 27; supplied by Beijing Chemical Reagent Co., China) were used as curing agents. The commercial SWCNTs (purity, ≥95%; diameter, 1–2 nm) were supplied by Beijing Cnano Technology Co., China.

In order to obtain the neat epoxy samples, the curing agent DETDA and MPD were mixed with epoxy resin, respectively, by using mechanical stirring at 800 rpm under 40 °C for 1 h. For the preparation of epoxy samples containing SWCNTs, the 0.5 wt% SWCNTs were dispersed in epoxy resin, and the mixture was mechanically stirred for 4 h and sonicated for 1 h to disperse SWCNTs uniformly in epoxy matrix. Subsequently, the DETDA curing agent was added and then the mixture was stirred at 800 rpm for 1 h. The ratio of epoxy/amine in each system was equivalent stoichiometric. After that, the above mixtures were degassed at 40 °C for 30 min under vacuum. Finally, the resin systems were poured into a steel mold, and then cured via a thermal cycle (80 °C for 0.5 h, 130 °C for 2 h, 170 °C for 3 h, and 200 °C for 1 h). After cooling down to room temperature with the oven, the tensile samples of different epoxy systems were obtained.

According to ASTM D638, the tensile performance of resin casts was tested by using a universal testing machine (Instron-1121, UK) with a testing speed of 2 mm/min to investigate the Young's modulus of different samples. To ensure the accuracy of the data, ten specimens were tested for every case and the average values were taken.

3. Results and discussion

3.1. Molecular dynamics investigation on modulus

In the calculation process of modulus, a total of three loading experiments were performed, in which the changes in the total energy of the configurations subjected to deformation were recorded stepwise along the x, y, or z directions. After an initial energy minimization, a small strain was applied to the configuration and then a second energy minimization was performed. By definition, the second derivative of the potential energy with respect to strain represents the stiffness of system. Accordingly, the stiffness matrix, C_{ij}, can be calculated by the following equation:

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

where σ_i and ε_j are the *i* component of the stress and strain tensors. The stiffness of matrix is calculated by averaging ten model structures for each epoxy resin matrix. For isotropic amorphous material, the stiffness