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Molecular dynamics simulation of cross-linked epoxy resin and its interaction energy with graphene under two typical force fields

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ABSTRACT

A model of cross-linked epoxy system composed of bisphenol-A resin, 2,3,6-tetrahydro-3-methylphthalic anhydride curing agent, and 2,4,6-tris(dimethylaminomethyl)phenol accelerator was established and molecular dynamics simulations were performed to calculate the properties of the epoxy and its composites. The results show that the mean square displacement (MSD) and glass transition temperature (T_g) calculated by Dreiding force field are always lower than that by PCFF force field, and the simulation results of Dreiding force field are better consistent with experiments. With the increasing simulation size, total MSD increases while T_g decreases slightly. The simulated systems with DGEBA more than 12 have T_g values similar to experiments. The molecular motion of epoxy system is also influenced by the cross-linking degree, and the presence of uncross-linked particles increases the total MSD. In the graphene/epoxy composites, interaction energy between modified monolayer graphene (MMG) sheets is larger than that between epoxy and graphene, indicating that MMG sheets tend to agglomerate when mixing with epoxy. Functionalization of graphene can reduce interaction energy between MMG sheets and increase that between epoxy resin and graphene, which is beneficial to the dispersion of graphene.

1. Introduction

Epoxy resins and epoxy-based composites have a wide range of applications in coatings, adhesives, aerospace, and electronics [1–4]. Generally, uncured epoxy resins have only poor mechanical, chemical and heat resistance properties. However, good properties can be obtained by reacting the linear epoxy resin with suitable curing agents to form three-dimensional cross-linked structures [5]. In industry, a large amount of epoxy resins are produced by combining epichlorohydrin and diglycidyl ether of bisphenol-A (DGEBA) to give DGEBA diglycidyl ethers, and DGEBA can be cross-linked by different curing agents, such as aromatic amines, acid anhydrides, phenols, cycloaliphatic amines, aliphatic amines, and thiols [1,3,5,6]. Each kind of resultant epoxy resins has quite different mechanical and thermal properties [3,6,7].

To study the properties of epoxy resins and epoxy-based composites, a lot of experimental and simulation work has been carried out. Compared with the time-consuming experiments with many limitations, molecular dynamics (MD) simulation has been widely used in the research of epoxy systems to calculate properties including radial distribution function (RDF), mean square displacement (MSD), glass transition temperature (T_g), coefficient of thermal expansion and so on [7–9]. Jeyranpour et al. [3] studied the influence of two curing agents, diethyltoluene diamine and etriethylenetetramine, on the DGEBA-based epoxy resin via MD simulation. Wu et al. [10] and Yang et al. [11] both suggested that the cross-linking density had great influence on the properties of epoxy system. In these MD simulations of epoxy resins, different force fields, such as Dreiding [7], PCFF [10], COMPASS [3], and ReaxFF [12], have been used. However, the comparison between force fields and the influence of simulation size were not studied.

Recently, the epoxy-based nanocomposites have received much attention from researchers. Li et al. [13] successfully built an interface model of a cross-linked thermoset polymer in the presence of a graphite surface and characterized the multilayer graphene reinforced epoxy composites. Hadden et al. [9] predicted that in the interface region of carbon nanofiber/epoxy composites, the molecular potential energy decreased with the cross-linking density of epoxy resin. Moreover, in our experimental work [14], it was found that the content of functional groups of thermally reduced graphene (r-GO) had great influence on the interfacial properties of r-GO/epoxy composites, which deserved further study.

In this work, an acid anhydride, 2,3,6-tetrahydro-3-methylph thalic anhydride (Me-THPA), was used as curing agent in MD simulations of fully cross-linked epoxy resin and the results were

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compared with our experiments [15]. 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30) was taken as the accelerator. Under two force fields, Dreiding and PCFF, cross-linked epoxy resins with four sizes were built to predict the structural and thermal properties. The influences of simulation size, force fields and cross-linking degree were systematically investigated by analyzing RDF, MSD and T_g. In addition, the interface region of graphene/epoxy systems was simulated. The interaction energy (E_{int}) between monolayer graphene (MG) and epoxy resin was calculated to study the effect of interfacial distance and functionalization degree of MG, which has instructive significance to experiments. In comparison, the E_{int} between two modified monolayer graphene (MMG) was also calculated.

2. Modeling and simulation methods

2.1. Molecular models of epoxy resin

The molecular structures of DGEBA, Me-THPA and DMP-30 are shown in Fig. 1(a). Under the influence of accelerator, DMP-30, the principal reactions between the DGEBA resin and Me-THPA agent are illustrated in Fig. 1(b). At first, the DMP-30 forms an ion pair with the Me-THPA. When the epoxy group is inserted into this ion pair, the carboxyl anion opens the epoxy group to form the ester bond while producing a new anion. This anion forms a new pair of ions with the Me-THPA. For convenience, the atoms to be connected with other reactants are named as co-atoms. For example, the carbon atoms of Me-THPA that are connected with nitrogen atoms of DMP-30 are called co-C. In experiments, the weight ratio of DGEBA, Me-THPA and DMP-30 was 100:85:1. Correspondingly, in the MD simulations, the molecular number ratio of DGEBA and Me-THPA was 4:7, and in every modeling system, the molecular number of DMP-30 was set to 1.

2.2. Cross-linking procedure of epoxy resin

In this study, molecular dynamics simulations of epoxy resins were carried out by the Accelrys Materials Studio 7.0 software. Dreiding force field [16] and Polymer Consistent Force-Field (PCFF) [17] were both used in the construction of crossed-linked epoxy resin for comparison. According to the principal reactions of DGEBA, Me-THPA and DMP-30, the following assumptions were made: (1) DMP-30 only works in the reaction that forms the first ion pair; (2) reaction occurs between a pair of co-atoms when their distance is within the reaction cut-off distance of 10 Å; (3) new covalent bonds are formed between the closest pair of co-atoms; (4) the epoxy systems are fully cross-linked. Furthermore, in the MD simulations, the van der Waals interaction was calculated by a cut-off distance of 15.5 Å, and the electrostatic interaction was calculated by the Ewald summation method with an accuracy of 1×10^{-4} kcal/mol; and the hydrogen bond interaction was calculated by a cut-off distance of 4.5 Å. There are five steps in the construction of cross-linked epoxy resin:

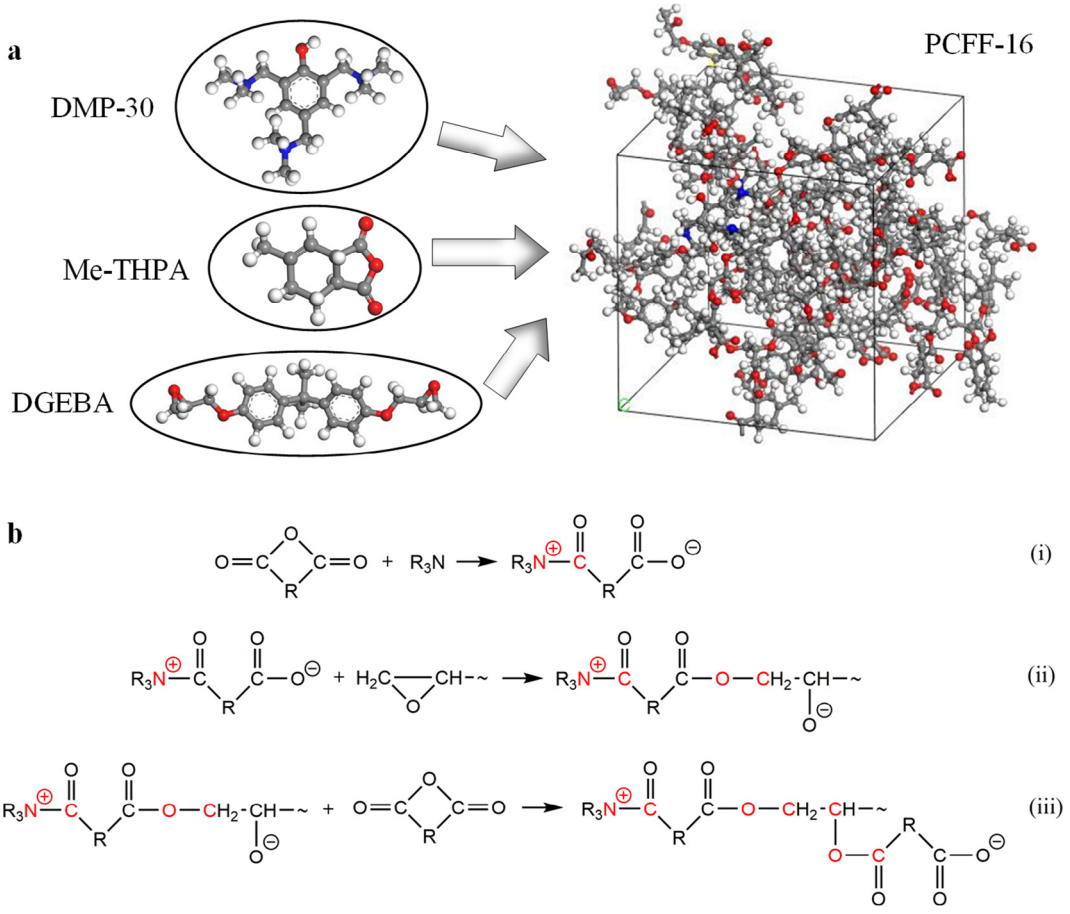

Fig. 1. Molecular models of DGEBA, Me-THPA, DMP-30, and PCFF-16 generated according to the cross-linking procedure: stick-ball models, balls with different colors represent different elemental atoms (red for oxygen, gray for carbon, white for hydrogen, and blue for nitrogen) (a) and the principal reactions of cross-linked epoxy system, in which the red atoms connected with other reactants are named as co-atoms (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)