



# A molecular dynamics study of water transport inside an epoxy polymer matrix



Sudharsan Pandiyan<sup>a</sup>, Jakub Krajniak<sup>b</sup>, Giovanni Samaey<sup>b</sup>, Dirk Roose<sup>b</sup>, Erik Nies<sup>a,\*</sup>

<sup>a</sup> Division of Polymer Chemistry and Materials, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

<sup>b</sup> Scientific Computing Research Group, Department of Computer Science, Katholieke Universiteit Leuven, Celestijnenlaan 200A, B-3001 Heverlee, Belgium

## ARTICLE INFO

### Article history:

Received 9 December 2014

Received in revised form 22 April 2015

Accepted 24 April 2015

### Keywords:

Molecular dynamics

Epoxy network

Water transport

## ABSTRACT

Classical all-atom molecular dynamics simulations were used to build and study a polymer network model of EPON-828 as an epoxy and diethylenetriamine as a cross-linker. A cut-off based cross-linking algorithm was adopted to make the cross-linking bonds of the epoxy network. A step-wise cross-linking process was implemented to achieve an epoxy polymer network with a maximum conversion of 0.8. Based on the uniaxial stress–strain response the elastic, bulk and strain moduli were determined and found to match with previous experimental and simulation studies. Water transport inside epoxy networks was analyzed by preparing the epoxy polymer network models containing different amounts of water. The water–epoxy hydrogen bonding interactions strongly influence the diffusion of water molecules in the polymer. Radial distribution functions, volume swelling analysis and mean squared displacements indicated two different types of water molecules in the polymer matrix. Water–matrix hydrogen bonding dominates during the initial sorption process and then the water–water interactions gradually increase their influence on the diffusion process by forming bigger water clusters.

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## 1. Introduction

Epoxy polymers are the products of the reaction between an epoxy resin and a so-called curing agent such as a polyfunctional amine [1]. The properties of the resulting thermosetting polymers from the epoxy–curing agent reactions are strongly related to the functionality of the monomers and the molar-ratio of epoxy and curing agent involved in the reaction [2,3]. Hence, by altering either the molar-ratio of the monomers or the functionality of the monomers the properties of the epoxy polymer can be fine-tuned [4,5]. For example, poly-functional amines lead to highly cross-linked polymers and the di-functional amines are generally used as chain extenders for producing linear polymers [6]. The cross-linked structure of the epoxy polymers leads to their higher mechanical strength and makes them important ingredient in various industrial sectors [7]. The global business of epoxy resin in year 2013 is US\$ 18.6 Billion and expected to grow to US\$ 25 Billion in next 5 years [8].

Epoxy polymers are mainly used as adhesives or as coating materials in different branches of industry ranging from bio-medical to aerospace [9,10]. In most of these applications,

the epoxy polymers are used to protect the inner layers of the composite materials from corrosion [11,12]. Moisture adsorption inside these epoxy polymer matrices is one of the major issues which leads to a lot of potential problems such as interfacial delamination [13,14], swelling [15,16], plasticization [17] and induced corrosion [18,19]. In order to make better polymers with higher protection capacity it is important to understand the underlying relationship between the polymer structure and the diffusion of small molecules. A number of experimental and simulation studies have been devoted to understand the moisture transport inside epoxy polymers [20–36]. However the molecular level understanding of the moisture induced plasticization effects are still an area of interest to many industrial processes. In the present work, we analyzed the water diffusion inside a bulk epoxy polymer matrix using molecular dynamics simulations and our intention is to shed some light on the plasticization effect induced by the moisture sorption at the atomistic level.

Previously, both experimental and simulation studies confirmed the presence of strong hydrogen bond interactions between the epoxy matrix and the water molecules [22,37]. Various experimental studies reported at least two types of water molecules namely, bound and free water molecules to be present in the system. The bound molecules are the ones found to have one or more hydrogen bond interactions with the epoxy matrix, the free

\* Corresponding author.

E-mail address: [erik.nies@chem.kuleuven.be](mailto:erik.nies@chem.kuleuven.be) (E. Nies).

molecules are the ones which are not having any specific interaction with the epoxy matrix [36–39].

Mijović and Zhang [34,35] investigated the interactions of water with the cross-linked epoxy polymer matrix using broadband dielectric relaxation spectroscopy and Fourier transform near-infrared spectroscopy and reported that three polar groups in the epoxy backbone (Hydroxyl, ether and the amines) are susceptible to make three different types of hydrogen bonds with the water molecules. They also studied the same systems using small-scale MD simulations of the network and reported the same kind of hydrogen bonding interactions in their model system as well. Dömötör and Hentschke estimated the excess chemical potential of water in the epoxy polymer matrix using the Widom test particle insertion method and studied swelling ratio in the epoxy matrix. Wunderle et al. [23] studied the moisture diffusion inside the epoxy matrix using experimental swelling measurements and MD simulation techniques as well. According to their report the fractional free volume, structure of the curing agent and the polar groups that are involved in the hydrogen bonding are the key components that influence the moisture diffusion. Wu and Xu prepared bulk epoxy matrices using MD simulations with varying concentration of water to analyze the mean squared displacements (MSD). They found that the epoxy matrices are indeed plasticized at higher water concentration (mass fraction of water,  $w_{\text{H}_2\text{O}} = 0.11$ ) resulting in an increased rate of diffusion of water in the polymer matrix. They also reported hydrogen bonding between the water hydrogens and the polar epoxy groups [22,40].

Though these studies shed some light on the water transport inside the epoxy polymer networks, understanding of moisture sorption induced plasticization effect at the molecular level is still lacking. Our objective in this study is to understand the water transport inside a bulk epoxy matrix and visualize the water induced plasticization effects at the molecular level. In order to achieve this, we need a realistic cross-linked epoxy network model. There are different strategies followed by various research groups to obtain cross-linked polymer network models. Yu et al. [41] used a completely cross-linked structure to represent the cured epoxy network and analyzed its interaction with alumina nano particle. Chiessi et al. [42] used a systematic packing technique to produce cross-linked hydrogels. Varshney et al. [43] controlled the reactivity of the curing agent to obtain different kinds of cross-linked epoxy networks. We choose the widely used cross-linking procedure to obtain network polymer structures [40,44–47], as this procedure is believed to produce more realistic and more accurate polymer network structure than the other possible methods [44]. The details of our simulation procedures, network preparation methodology and production run details are presented in Section 2. In Section 3 the validation of the network structure, evolution of the largest molecular cluster as a function of conversion and the analysis of the mechanical properties of the fully cured epoxy network are reported. The water transport inside the epoxy network, volume swelling induced by the water sorption, water cluster formation inside the epoxy matrix and the effect of water sorption on the mechanical properties of the epoxy network are discussed in section 4. Section 5 summarizes the conclusions.

## 2. Simulation details

The chemical structures of the epoxy and the poly-amine considered in our simulations are shown in Fig. 1. DETA molecule has five active hydrogens that can involve in chemical cross-linking to form an epoxy network. EPON-828 has two terminal epoxide groups that can react with the DETA molecules. A stoichiometric ratio of 5:2 between DETA:EPON-828 was taken in all our simulations.

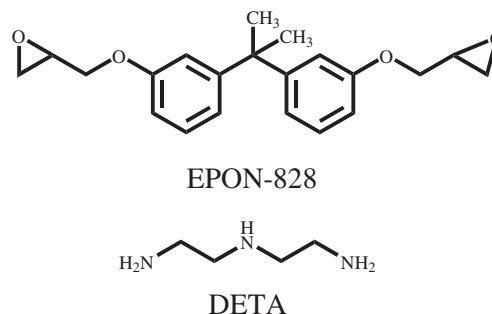


Fig. 1. Chemical structure of EPON-828 and diethylenetriamine (DETA).

All bonded and non-bonded interaction parameters for the starting materials as well as the final network were taken from the OPLS-AA force field [48]. For the water transport studies, the SPCE water molecule model was used in this study [49]. The partial charges on the monomeric atoms were calculated using GAUSSIAN-09 [50] package with a B3LYP/6-31G(d,p) level of theory. The charges on the cross-linking atoms were adjusted based on their bonding order, as the primary nitrogen becomes secondary and tertiary carbon during the cross-linking procedure. The electrostatic potential fitted partial charges were used in all the simulations. Particle mesh Ewald summation method [51] was used for coulombic interactions with a cut-off distance of 1.2 nm. The same cut-off distance was used for van der Waals interactions and the long range correction for pressure and energy were also included.

All the simulations were carried out using the GROMACS v4.5.3 MD simulation package [52]. The leap-frog algorithm with a time-step of 1 fs was used in our simulations. The Berendsen barostat [53] with a coupling constant of 0.5 ps and the velocity rescaling algorithm [54] with a coupling constant of 0.1 ps was used for pressure and temperature coupling in all our *network preparation* steps. The Parrinello–Rahman barostat [55] with a Nosé–Hoover thermostat [56] were used for the *production run* simulations with the same couple constants.

### 2.1. Network preparation

The steps involving the preparation of cross-linked epoxy polymer network are given below.

#### 2.1.1. Step 1: Creation of equilibrium mixture of EPON-828 and diethylenetriamine (DETA)

Five different initial starting configurations of the mixture before cross-linking were prepared. A mixture containing 215 epoxy molecules with 86 DETA molecules was annealed at low density and 1000 K for a duration between 1 and 5 ns. Snapshots picked at 1, 2, ..., 5 ns were used as starting configuration for the next steps in the simulation. The different high temperature configurations were cooled down to room temperature at a rate of 1 K/ps. Once at room temperature, all the systems were allowed to relax under 0.1 MPa pressure under NPT conditions for 5 ns to obtain the equilibrated samples. The equilibrium simulations were validated by determining the dihedral correlation functions, the end to end distances and the radii of gyration of the epoxy molecules. The final configuration after the 5 ns simulation was further considered for the cross-linking procedure.

#### 2.1.2. Step 2: Cross-linking based on cut-off distance criteria

The flow diagram of the cross-linking procedure is presented in Fig. 2. The iterative procedure started with an equilibrated mixture of uncross-linked epoxy and amine mixture obtained in step 1. A

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