Atomistic simulation study of absorbed water influence on structure and properties of crosslinked epoxy resin

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Abstract

Absorbed water can generally degrade most polymer materials with many desired thermal and mechanical properties. In this work, a series of two-step molecular dynamics simulations have been carried out to study the moisture effects on an epoxy-amine polymer network. Copolymer of diglycidyl ether bisphenol A (DGEBA) and isophorone diamine (IPD) was investigated together with its four moist networks with concentrations of water 1.30, 2.54, 5.02 and 11.5 wt%. Simulated results clearly indicated that with addition of water molecules the density of the polymer system decreases whereas the mobility of the network chains increases at higher water concentration. However, at lower water concentration the results present the contrast trends. These differences resulting from water presence can be attributed to the interplay between the hydrogen bonding interactions and the free volumes, the former is responsible for antiplasticization whereas the latter leads to plasticization of the polymer materials. Further analysis confirms that the networks form hydrogen bonds with absorbed water molecules, which preferred to locate in the vicinity of polar groups on the polymer network, and water at higher concentration can cluster with each other. The diffusion coefficient increased with increasing water concentration; the same trend as the change in fractional free volume but contrary to that in density. These results from our simulations were in good agreement with the general experimental observations and the free volume theory.
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Keywords: Atomistic molecular simulations; Absorbed water; Crosslinked epoxy resin

1. Introduction

When used as structural materials, polymers generally exhibit many predominant performances superior to the conventional materials, for instance, having similar excellent thermal and mechanical properties but much cheaper and lighter than metals and not more fragile than ceramics. Besides, polymers can be widely used as "soft materials", in coatings and adhesives, which are not so in the cases of metals and ceramics. So the polymers have been substituting the latter in more and more practical fields. However, most polymers also suffer from some common disadvantages, one of which is that once they come in contact with water they would become swollen and significantly degraded. The barrier properties of the coatings and hygrothermal aging of the materials are also closely associated with the absorbed moisture. Therefore, the variations of these properties of polymeric systems as a function of water content have been extensively studied "macroscopically" by many experimental methods, yielding several hypotheses about the role of water in the polymers. However, understanding "microscopically" the effect of water on the structure and properties is very critical to modify the structure of the polymers to tailor their properties.

Recently, crosslinked epoxy resin systems have attracted us with much interest, mainly due to their excellent collective performances and very widespread applications [1−3]. Like most polymers, however, this kind of polymer has the potential of being exposed to a humid environment and susceptible to the moisture sorption, which is well known to usually cause plasticization and diminish the thermal and mechanical properties. Absorption [4−12], diffusion [13−16] and transportation [17−20] of water in crosslinked epoxy resins have been

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widely studied since they are related to the changes in the structure of the polymers and in the interactions between water and polymers. The swelling of the crosslinked epoxy resins under the wet environments has also been investigated [21–22]. It can be inferred from many advanced experimental methods [4,13–16,23–26] that water tends to form hydrogen bonds with the polar groups on the polymer networks and water in the crosslinked epoxy resins has double nature: free water and bound water, and the former is much easier than the latter when desorbed.

Despite the extensive experimental and theoretical studies, several molecular simulation studies have been also attempted [27–30]. Domotor and Hentschke [27] studied equilibrium swelling of an epoxy resin in contact with water, determining equilibrium water content and the swelling ratio. Yarovsky and Evans [28] studied the mobility of water in two low-molecular weight crosslinked epoxy resins, obtaining the right trend of diffusivity of water in these systems. By contrast, Lin and Chen [29] investigated moisture diffusion in a high-molecular-weight crosslinked epoxy resin, assisting in the verification of the experimental diffusion coefficients and desorption activation energy. Mijovic and Zhang [30] systematically studied the motion and interactions of water in a classical epoxy-amine network, identifying three types of hydrogen bonds and their destinations and dynamics. All these simulation studies mainly focused on water in the polymer matrix and in some degree can contribute to understanding moisture effect on epoxy polymer networks. However, these plasticization effects remain incompletely understood. And, somewhat surprisingly, more direct simulations on the epoxy networks themselves under moisture environments remain unperformed. If these simulations can reproduce those experimental macroscopic effects, they can be directly related to detailed microscopic information generated from the simulations (in particular, molecular dynamics simulations) themselves. This would be of great desire since such a correlation between the two scales can be used to develop more accurate theories towards the development of better epoxy products with improved barrier property and swelling property.

As a matter of fact, molecular simulations at atomistic level have been successfully applied to study the diffusion and permeability of water molecules in various linear homopolymers and copolymers [31–36]. In this paper, we reported such a molecular simulation study, which marks for the first time that atomistic molecular simulations has been employed to study structure and properties of the whole water-network system. Epoxy model systems containing various water contents would be considered and compared with each other. The same to Mijovic's work [30], the focus was not on a particular material but rather on a generic group of polymer networks and hence the choice of an epoxy-amine formulation was convenient. These results provide a detailed insight into the structure–property relationship of the polymer systems.

1.1. Simulation details

Most of this work was performed on one HP xw4300 workstation using Material Studio 4.0 software (compared to its earlier Unix edition Cerius2) purchased from Accelry Inc (formerly Molecular Simulation Inc). And the potential functions used in the calculation of energies and forces were advanced COMPASS described elsewhere [37] except that the model construction used simple Dreiding2.21 forcefield in Cerius2 to optimize and mix the two components.

A series of molecular models of the systems were used to represent realistic epoxy systems with and without water. The crosslinked epoxy system based on diglycidyl ether bisphenol A (DGEBA) and isophorone diamine (IPD) was studied. The chemical structure of these two components is summarised in Fig. 1. Briefly, the amorphous polymer model was dynamically built by making some reasonable assumptions. Firstly, 16 epoxy segments and 8 hardener segments containing reactive sites were packed into a 3D periodic cell box according to self-avoiding random-walk method of Theodorou and Suter; this formulation was then mixed by using molecular dynamics (MD) after an initial energy minimization (MM) based on generic Dreiding2.21 forcefield; under close proximity, covalent bonds were formed between the nearest reactive pairs and reaction cutoff distance considering removal of ring catenation or spearing; repeating MM and MD and forming bonds for several times, a crosslinked polymer network with a conversion of 93.7% was finally obtained for an initial configuration of dry network. This procedure was in detail described in one of our previous papers [38]. In the resulting model system with cell dimension 21.55 Å × 21.55 Å × 21.55 Å, there are only two free (unreacted) hydroxyl groups and one free amine group with two hydrogen atoms.

After a long optimization and initial relaxation on the dry network, i.e. 10,000 steps of energy minimization and 100 ps (1 ps = 10^{-12} s) of NVT at 600 K, the same MD procedure to Bharadwaj's [39] to investigate the effect of water on the diffusion of N_2 in PMMA was taken. An NPT ensemble dynamics with 500 ps was firstly carried out at 0.1 MPa and 600 K. The instantaneous density was observed to fluctuate about a well defined mean over the time scale of the dynamics, indicating that the equilibrium density for the given temperature and pressure had been attained. A configuration with the density closest to the equilibrium value was then used to initiate NVT ensemble dynamics for a period of 2 ns (1 ns = 10^{-9} s). The last configuration in the proceeding step was chosen for randomly inserting five water molecules into the cavity of the periodic system while keeping some distance from each other. The resultant moist network system was subject to the same "thermal history" as for the dry network. According to the same strategy, 10, 20 and 50 water molecules were added into previous less-water system step by step. Initial energy minimization and dynamics relaxation were followed by the two-step molecular dynamics simulations (NPT and NVT). One snap of every moist network is also collectively shown in Fig. 1. The simulation cells containing 5, 10, 20 and 50 H_2O molecules correspond to the four concentrations of H_2O, i.e. 1.30, 2.57, 5.02 and 11.5 wt%.

As an initial study, only 600 K was arbitrarily chosen. This somewhat higher temperature may correspond to a virtual glassy state considering the density according to a related
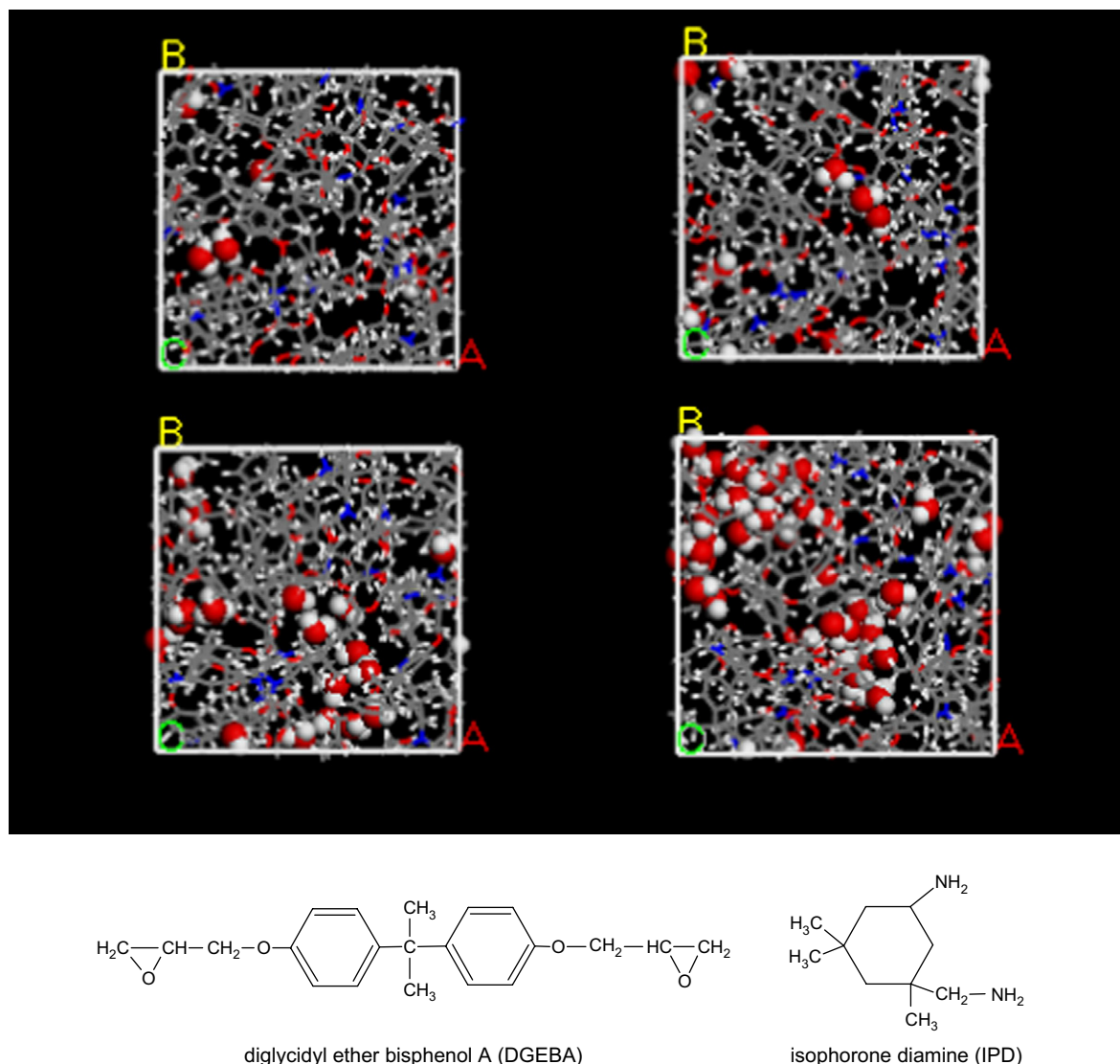
diglycidyl ether bisphenol A (DGEBA)

isophorone diamine (IPD)

Fig. 1. Schematic representation of the unit cell models of the four epoxy-amine polymer networks containing water molecules (top left: 1.30 wt% H_2O, top right: 2.54 wt% H_2O, bottom left: 5.02 wt% H_2O, bottom right: 11.5 wt% H_2O). H_2O molecules are represented in CPK models and the epoxy networks are represented in line models. And schemed are molecular structures of the two monomers (bottom left: resin component DGEBA; bottom right: hardener component IPD).

study. Therefore, the behavior at this temperature can be related to that at room temperature. Moreover, it can give rise to faster movements to equilibrated states where a better statistical sampling of the conformational space would be obtained. The thermostat is due to Andersen [40]. For pressure control, Berendsen method [41] was used. Time step of 1 fs (1 fs $= 10^{-15}$ s) and Velocity Verlet algorithm were kept for the integration of atom motion equations. In terms of non-bonding interactions, advanced Ewald summation and Cell Multipole Method (CMM) were selected for Columbic interactions in the NPT and NVT ensemble dynamics, respectively, whereas atom-based cutoff of 9.5 Å and a butter of 0.5 Å were employed for van der Waals interactions in both simulations. These choices of simulation parameters generally result from the balance consideration among accuracy and efficiency of computation. Specifically, a related study indicates that the atom-based cutoff method cannot properly treat the long

electrostatic interactions of the infinite systems. Because of the infinite feature, group-based cutoff also cannot be employed. Several different initial configurations were employed for the dry polymer network and resulting moist network, and similar results were found. Therefore, only one result from some initial configurations is reported in next section.

2. Results and discussion

2.1. Density of the whole system

Density is one of the most important characteristics of packing mode and structure of bulk polymeric materials. Moreover, the diffusion coefficients of small molecules and other properties (such as tension and shear modulus and glass transition temperature, T_g) of polymer materials are very sensitive to the density. Considering the importance and no

corresponding experimental data available, the densities were firstly calculated for the five model systems and compared with each other. The NPT MD simulations used are common and prove of great value in reproducing reasonable experimental data (volumetric properties) for many other polymer systems [42]. The time-averaged densities (the last 300 ps out of all 500 ps) of the DGEBA-IPD systems at all H_2O concentrations and at 600 K are shown in Table 1. The simulated density displays an initial slight increase at lower water concentration followed by a strong drop at higher water concentration. The initial increase can primarily result from additional specific interactions, whereas the following decrease can be considered as the consequence of plasticization of the polymer matrix. These contents will be described in detail later. An initial increase followed by a strong drop in density has also been reported for polyamide 6,6 with addition of water [43]. But for PMMA system, the change in density exhibited a negligible decrease at lower concentration of water [39]. The former presenting a stronger hydrogen bonding ability than the latter seems to support our arguments. The water concentration in other systems can be too low to observe any initial increase in the density. As noted above, no corresponding experimental data are available for this high temperature (600 K) on these systems for a direct comparison. Actually, our polymer network model and forcefield have some difference with the realistic system although the calculated densities and elastic constants compare reasonably with the corresponding experimental data (as shown in our previously published article, [38]). Therefore, this paper intended to present the relative comparison but not completely the absolute values.

2.2. Specific interactions

Specific interactions involved in the studied system were examined by calculating radial distribution functions (RDFs) of atoms of interest. These functions, also referred to as pair correlation functions, provide insights into the structure of those model systems studied. For two groups of atoms, denoted by A and B, in a cell with volume V, they can be determined by [44]

$$g_{AB}(r) = \frac{V \times \left\langle \sum_{i \neq j} \delta\left(r - |r_{Ai} - r_{Bj}|\right) \right\rangle}{(N_A N_B - N_{AB}) 4\pi r^2 dr} \quad (1)$$

Table 1
Diffusion coefficients (D) of H_2O, the densities (ρ), total volumes and fractional free volumes (Ffv) as a function of H_2O concentrations of the four cell systems at 600 K

wt% of H_2O	ρ, g cm^{-3}	V, Å^3	D, 10^{-5} cm^2 s^{-1}	Ffv
0.00	1.044	10869.6	–	0.3915
1.30	1.048	10936.9	1.06	0.3871
2.54	1.032	11252.8	1.30	0.3959
5.02	1.025	11625.2	2.21	0.3997
11.5	0.965	13274.7	2.99	0.4325

where i and j refer to the ith and jth atoms of group A of N_A atoms and group B of N_B atoms and N_{AB} is number of atoms common to both groups A and B, angle brackets imply averaging over different configurations. For a single group of atoms, accordingly, Eq. (1) can be reformulated as

$$g(r) = \frac{V \times \left\langle \sum_{j \neq i} \delta\left(r - |r_{ij}|\right) \right\rangle}{(N^2 - N) 4\pi r^2 dr} \quad (2)$$

these functions give the probability of finding an atom at a distance r from another compared to the ideal gas distribution [45], that is, completely random distribution. Insofar, they give a way to infer interactions between atoms or groups and to analyze the role of water in the polymer systems.

Shown in Fig. 2 are intermolecular RDFs for the pair of interest, that is, the polar atoms (such as oxygen and nitrogen atoms) on the network and oxygen atoms on water molecules. It can be expected that these correlation functions provide the most important information about polar interactions between water and the polymer networks. The four moist networks display similar characteristics: there are two obvious peaks at distances of 2.75 Å and 5.02 Å. The sharp peak at 2.75 Å is an indication of the presence of hydrogen bonds whereas the broad peak at 5.02 Å can be associated with the symmetry of polar groups on epoxy and amine segments on the networks. The shorter distance (2.75 Å, the peak positioned) also indicates that the absorbed water molecules are more likely to be located in the vicinity of the polar groups on the polymer network. Interestingly note is that the correlation function at middle water concentration is higher than those both at one low concentrations and three high water concentrations. This fact indicates that the probability or the strength of forming hydrogen bonds initially increases with increasing water but decreases beyond a certain value of water concentration. The reason is that the number of polar groups on the networks available for hydrogen bonding is unvaried with
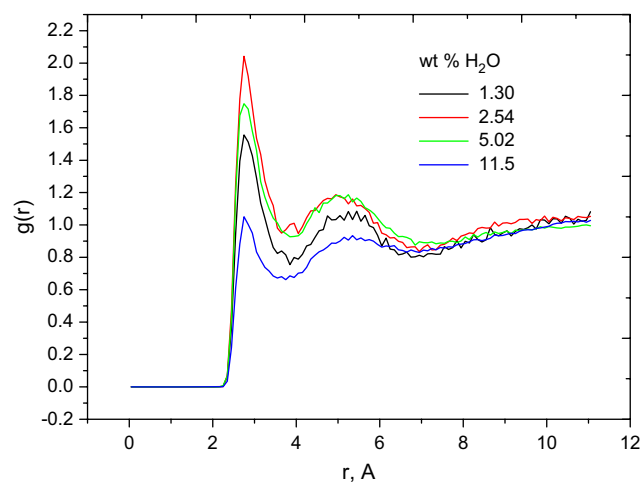

Fig. 2. Intermolecular radial distribution functions between polar atoms on four moist epoxy networks and oxygen atoms on water molecules with water concentration as a parameter.

addition of water molecules, and when these polar groups are saturated by some water, additional water prefers to form hydrogen bonding with another water molecule but not with the polar groups on the network. This truly indicates the appearance of water molecule clusters at higher water concentration. These qualitative results from radial distribution functions comply with those from the geometric criteria of hydrogen bond for other epoxy-amine system [30].

In Fig. 3 is shown the intermolecular RDFs between oxygen atoms on water molecules at the four concentrations 1.30, 2.57, 5.02 and 11.5 wt% H_2O. It can be seen that one water molecule is systematically departed from another molecule at a distance of 2.85 Å (a bit bigger than 2.75 Å), indicating the presence of hydrogen bonds with a bit difference from those formed between water and the polymer network. It can be seen that the probability of forming hydrogen bonds monotonously drops with the addition of water molecules. This can provide another proof that water molecules tend to cluster each other at higher water concentrations. Inferred from these results, the RDF of oxygen atoms in the pure water is lower than that on the water molecules at any water concentration of wet polymer network systems, which is consistent with the simulation result on other polymers presented by Tonsing and Oldiges [46].

The total RDFs between polar atoms on the polymer networks were also presented in Fig. 4, which are divided into three groups: hydroxy oxygen−ether oxygen (I), hydroxy oxygen−nitrogen (II) and hydroxy oxygen−hydroxy oxygen (III). They confirm the presence of hydrogen bonds in all the polymer systems and indicate different hydrogen bonding structures (and polar interactions): type III has only one class of regular hydrogen bonds whereas types I and II have one class of regular hydrogen bonds (2.75−2.85 Å) and one class of twist hydrogen bonds (3.05−3.15 Å), and in type I the regular hydrogen bonds are more than the twist hydrogen bonds whereas in type II the regular hydrogen bonds have the probability similar to the twist hydrogen bonds at lower water
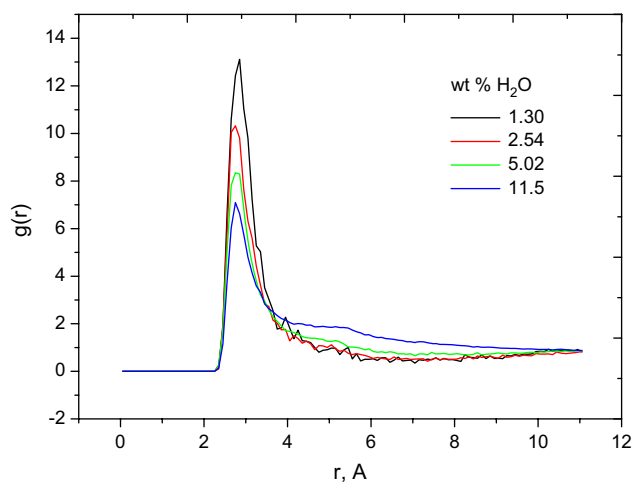

Fig. 3. Intermolecular radial distribution functions between oxygen atoms on H_2O molecules involved in the wet epoxy networks with water concentration as a parameter.
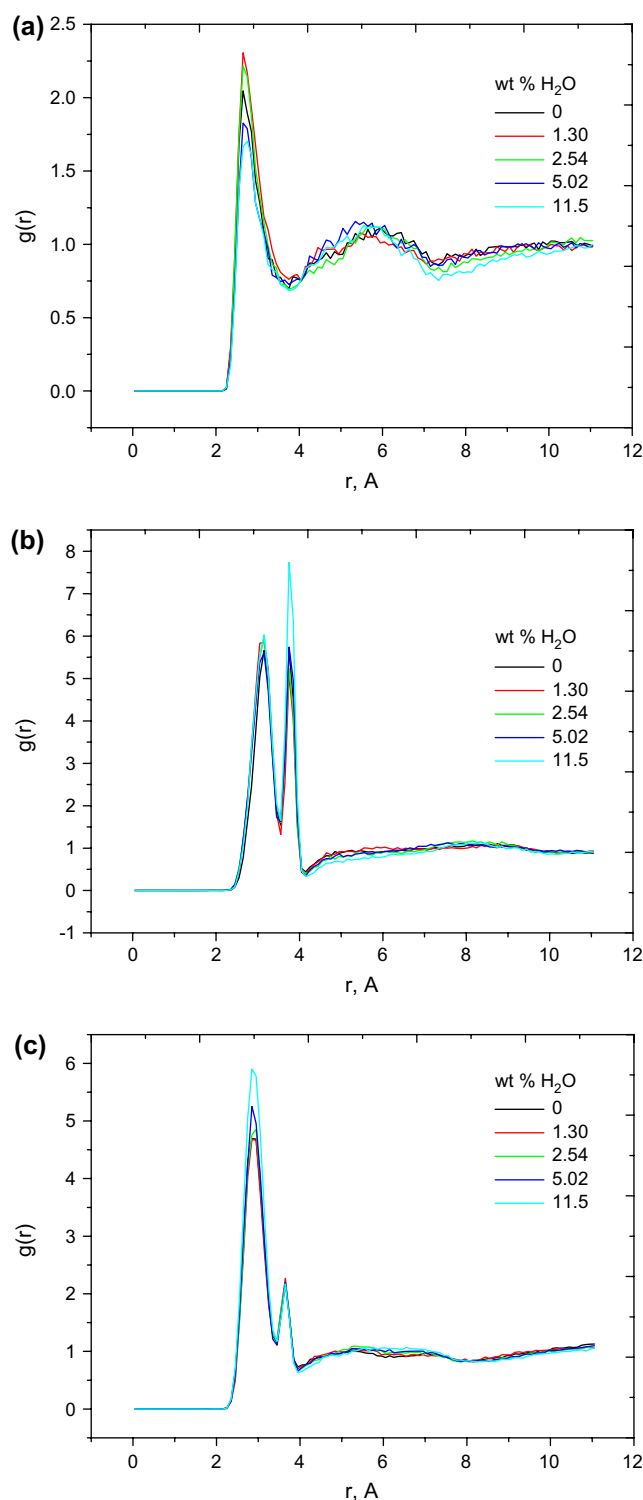

Fig. 4. Pair correlation functions of polar atom pairs involved in the epoxy systems: (a) hydroxy oxygen−hydroxy oxygen; (b) hydroxy oxygen−nitrogen and (c) hydroxy oxygen−ether oxygen.

concentration and even lower than those at higher water concentration. In general, within the three lower concentrations studied, they present only slight change, among which a relatively more clear difference is found in the RDFs of hydroxyl oxygen−hydroxyl oxygen atom pairs. The shape and location

of the peaks in this RDF are very similar to those between water and polar atoms on the polymer network, which can provide another proof that the broad peaks results from the symmetry of polar groups on epoxy segments. For the highest water concentration, all the three types of RDFs reveal more obvious hydrogen bonding interaction features: types I and II become higher whereas type III becomes lower. Noted that intra-molecular hydrogen bonds in amine-cured epoxy system have been detected by Fourier transform infrared spectroscopy (FTIR) [47]. Nevertheless, various hydrogen bonding structures discussed here were very hard to distinguish by this experimental method.

2.3. Diffusibility of water molecules

The diffusibility of water molecules in the polymeric networks is discussed in this section. As noted above, diffusion of water molecules in other polymer systems is one of the most active study areas because these investigations of diffusion of H_2O in the polymers can provide some useful information concerning structure and properties of the polymer itself. Most of these studies were devoted to the diffusion coefficients of constant water content but seldom on the effect of water content on diffusion constant. Without doubt, water content has some effect on its diffusion coefficient since the environment around water varies from one concentration to another concentration, in other word, more water–network interactions are displaced by more water–water interactions with addition of more water molecules. In order to assess this effect, the self-diffusion coefficient was calculated for water molecules in the four moist networks. In the long time, the self-diffusion coefficients of H_2O can be readily computed from the Einstein relation:

$$D = \frac{1}{6}\lim_{t \to \infty}\frac{\mathrm{d}}{\mathrm{d}t}\langle|\overrightarrow{R}(t) - \overrightarrow{R}(0)|^2\rangle \tag{3}$$

where $R(0)$ and $R(t)$ are the atomistic positions of the center of mass at initial time 0 and later time t, respectively, and the part in angular bracket denotes mean-square displacement (MSD) of all atoms involved in given water molecules, which can be reformulated as follows:

$$\mathrm{MSD} = \frac{1}{3N}\sum_{i=0}^{N-1}\langle|\overrightarrow{R}_i(t) - \overrightarrow{R}_i(0)|^2\rangle \tag{4}$$

where N is the sum of atoms of the model system involved in the calculations, the angular bracket has the same meaning as in Eq. (3), denoting averaging over all atoms of the type and the simulation time origins.

The log–log plot shown in Fig. 5 displays typical diffusion behavior of H_2O in the moist polymer [39,48]: anomalous diffusion at short time scales, where water spends much time sampling local free volume in the polymer matrix; the Einstein diffusion regime at longer time scales, where water executes random hops over several free volume sites; statistic noisy regime at last times due to fewer time origins for averaging. The
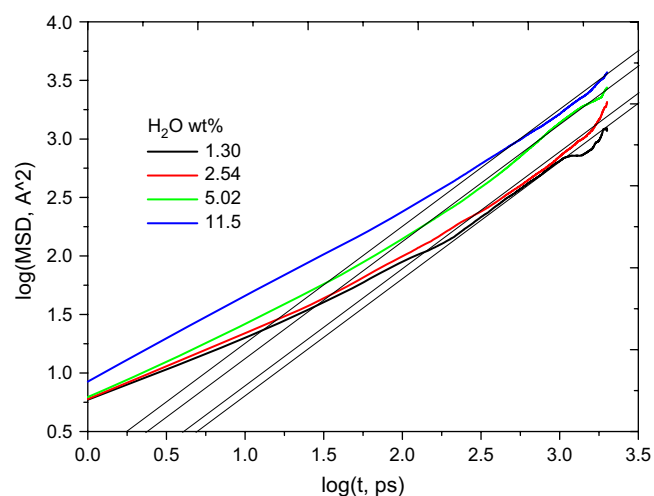

Fig. 5. Log–log plot of mean-square displacements vs simulation time for H_2O in moist DGEBA-IPD networks at four different concentrations at 600 K. The lines represent that slope = 1 fits to the true diffusion regime.

true diffusion regime corresponds to slope = 1 fitting line to each of the above curves as shown in Fig. 5. The diffusion coefficients from the intercept log(6D) are also shown in Table 1. Experimentally, the diffusivity of water in the epoxy/amine system TGDDM/DDS was found to increase with total water concentration [18]. And there are no experimental data for the diffusion coefficients of water in DGEBA-IPD network. To say the least, once again, an absolute comparison to the corresponding experimental data requires more realistic molecular models (bigger cell dimension, more complete conversion and more accurate forcefield). It should be noted that when the diffusion coefficient becomes higher at relatively higher water concentration the true diffusion regime becomes more clear and includes longer time range due to averaging upon more water molecules. The so-obtained diffusion coefficients here followed Bharadwaj's method [39]. Although somewhat artificial, this method obtains a proximate value, and more importantly the reasonable trend: the diffusion coefficient increases with increasing concentrations of H_2O molecules. From this behavior it can be understood that there is bigger fraction of free water with weaker or no hydrogen bonding to the polymer network at higher water concentration as suggested by many experiments [13,14,25]. Besides the concentration of water, water cluster can also affect the diffusion coefficients in the polymer network. It should be noticed that, in the studied system with strong polarity [48], water cluster cannot be too big to significantly affect the diffusion coefficients. It is true at all levels of water content that the majority of absorbed water molecules reside in the network as single molecules as pointed out by Mijovic and Zhang [30].

2.4. Fractional free volumes of the model systems

The differences in the diffusibility of a fraction of H_2O generally reveal the change in the free volumes in the four studied epoxy systems available for diffusion of H_2O molecules. The

whole periodic cell models comprise of occupied volume parts and free volume parts, which are separated by some surface, simply, the van der Waals surface of polymer chains and water. The free volumes for the last 1000 configurations from NVT MD simulations were calculated and averaged for each water concentrations using QSAR module in the Material Studio 4.0. Then the fractional free volumes can be calculated as the ratio of free volumes to the total cell volumes. The results are also shown in Table 1. Initial decrease followed by monotonous increase in the fractional free volumes is observed, which takes an exact contrary rout to the changes in the densities. Table 1 also shows that the diffusion constant is increased with the fractional free volumes. When a fraction of water is added, the increase in the total volume is relatively lower. However, when more water is absorbed into the network, the total volume rise up very quickly, companied by plasticization of the polymer network. Besides the fractional free volumes within the systems, the distribution of the free volumes as well as structure and dynamics of polymer network is also known to affect diffusivity significantly. Although to include all these aspects and their relationship in a study is very amazing, but not impossible; fractional free volume can be used as a first fast check of diffusibility and even permeability of a polymer system or other systems.

2.5. Local dynamics of the polymer network chains

Investigation of the change in the dynamics of the polymer network chains under different water concentration is very critical to understand the plasticization effect of water molecules on the polymer system. Considering the smaller systems and the relatively narrower concentration range, the effects of different water concentrations on global structure and dynamics are expected too small to be detectable in the present simulations. Therefore, investigation of local structure and dynamics can be more meaningful. It is also recalled that water molecules prefer to locate in the vicinity of polar atoms or groups, which means that the effect of water molecules on these atoms or groups is more impact than on non-polar atoms or groups. In particular, we will focus on the translational motions of the polar atoms and rotational motions of the "polar covalent bonds". The former was examined by calculating the MSDs of the atoms according to Eq. (4) whereas the latter was examined by calculating the rotational time correlation function of the polar covalent bond vectors (denoted by polar vectors) according to the following relation

$$P(t) = \langle u(0) \cdot u(t) \rangle \qquad (5)$$

where u is an unit polar vector and the part of the angular bracket denotes averaging all time origins and the like vectors in the model systems.

By the difference in and around environment, three classes of polar atoms were separately calculated: (1) hydroxy oxygen atoms, (2) ether oxygen atoms and (3) nitrogen atoms. Similarly, three classes of polar vectors were separately calculated: (1) the H−O vector, connecting the hydroxyl hydrogen with

the hydroxyl oxygen, (2) the N−C vector, connecting the nitrogen and neighboring carbon, and (3) the O−C vector, connecting the ether oxygen with ether carbon. The calculated results are collectively represented in Fig. 6, where the former three sub-curves are MSDs whereas the latter three sub-curves are vector autocorrelation functions (VACF). For all the three MSDs (latter parts in the curves as well as those in $P(t)$s were excluded from the following analysis due to statistic noise), similar features are generally found: at the two lower water concentrations, translational motions of the polar atoms are reduced where the difference in the behaviors at these different water concentrations are hard to distinguish; at the higher water concentration, these motions are clearly enhanced. The three $P(t)$s also show the similar trend to the three MSDs: rotate faster at higher water concentration and rotate slower at lower water concentrations compared to that under the condition without water, which can be compared to that obtained by Mijovic and Zhang [30]. All these results roughly indicate the different effects of water on dynamics of polymer network chains at various water concentrations.

To be a short summary, water has a double effect on the polymer networks depending upon its concentration. On one hand, the increase or decrease in the motions of polymer network chains can result from the differences in the free volume and in the specific interactions described above; on the other hand, the increase in the motions of polymer network chains would lead to the degradation of many physico-mechanical properties such as density, and tensile and shear modulus according to the elementary rubber elasticity theory [49]. Specially, the bond vector autocorrelation functions have been used to examine the flexibility of the polymer chains, which affect significantly the T_gs of the polymers [50,51]: the more flexible the polymer chains the lower the T_gs are. On contrary, the decrease in the chain motions would lead to the enhancements of these properties otherwise. Interestingly, we noticed that the non-monotonic behavior covered here was almost same to the one recently published by Dirama and coworkers [52] for mixtures of two low molar mass compounds, glycerol and trehalose. These results seem to indicate that there exists an optimized formulation where hydrogen bond interactions play the most important roles in the properties of the multi-component systems. Nevertheless, this requires some further confirmation from both experiments and simulations to our system.

3. Conclusions

This work reported the results of explicit MD simulations of one dry and four wet epoxy-amine crosslinked networks based on DGEBA and IPD. Atomistic models allow us to obtain much detailed information about structure and properties of these systems, which are not available for any coarse-grained models. Although only relatively narrower range of water concentrations was considered, some main features related to the effect of water concentrations were confidently captured:
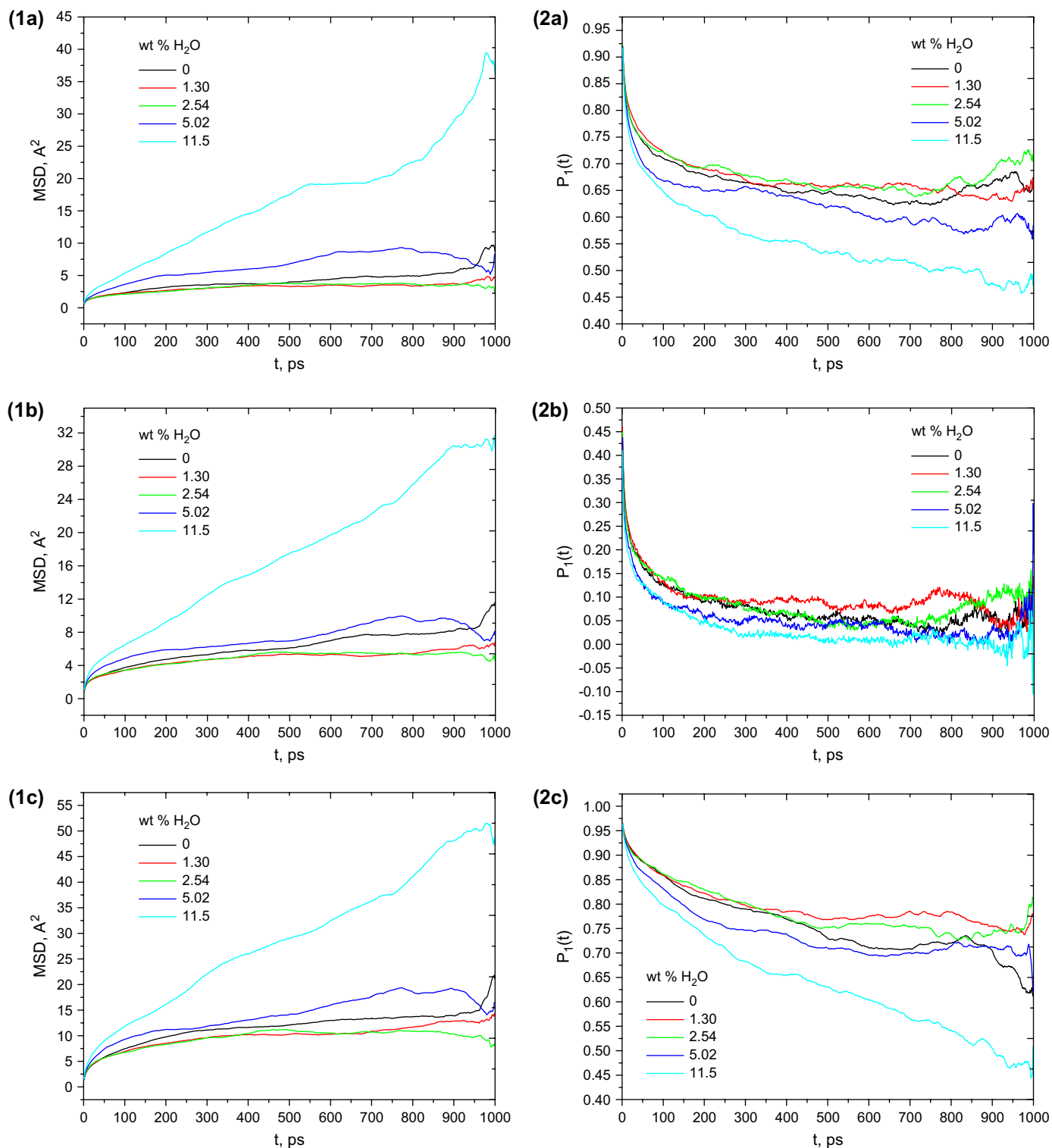
Fig. 6. Mobility of polar groups involved in the epoxy systems. Mean-square displacements (MSD) as a function of simulation time for polar atoms: (1a) nitrogen atoms; (1b) ether oxygen atoms; (1c) hydroxy oxygen atoms. Rotational time correlation functions (P_1) as a function of simulation time for polar valence bonds: (2a) O−C vector; (2b) O−H vector and (2c) N−C vector.

(i) When more water was absorbed, where water molecules can cluster each other, the polymer system was plasticized, that is, the density was reduced, fractional free volume was increased which was further confirmed by the increase in the diffusion coefficient of water, and thus the polymer network chains became more flexible which would lead to degradation of other thermal and mechanical properties.

(ii) When less water was added, the polymer system was antiplasticized, that is, those properties referred above would present the contrast trends. Specifically, the initial increase in the density of the polymer system was attributed to the specific hydrogen bonding interactions involved in the systems. Further analysis also indicated that water preferred to locate in the vicinity of polar groups on the networks.

All these results comply with general experimental observations, which means that the used model and forcefield are valid, at least in obtaining the right trends of water effect on the polymer systems. This work represented the first step to more intensive studies of water plasticization effects on the polymer networks.

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