

Molecular Dynamics Simulation Study of Motions and Interactions of Water in a Polymer Network

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Molecular dynamics simulation was conducted of the interactions and dynamics of water in a fully cured stoichiometric epoxy-amine network with moisture content ranging from 0 to 4.75 mol/L (0 to 8 wt %). Three types of hydrogen bonds (HBs) were identified in the dry network. Each of those three HBs involves hydrogen of the network hydroxyl group (HO) and one of the three acceptors: oxygen of the network hydroxyl group (OH), oxygen of the network ether group (OC), or nitrogen of the network tertiary amine (NC). The majority of the absorbed water molecules are located in the vicinity of the polar groups on the polymer network. The absorbed water breaks up some of the initially present HBs and forms new ones, both with the network groups and with other water molecules. The total number of HBs per one water molecule reaches 1.6 at 3.80 mol/L (6 wt %) moisture content, well below the value of 3.26 for bulk liquid water. The orientational motion of the absorbed water is anisotropic: the rotation of the vector μ , which lies in the direction of the dipole moment, is considerably slower (more than two decades) than the rotation of the vector that connects two hydrogen atoms and/or the vector perpendicular to the plane of the water molecule. The calculation of the time autocorrelation function for various HB pairs confirms that hydrogen bonding between the water oxygen and the hydrogen of the network hydroxyl group is at the heart of the observed slowdown in the dynamics.

1. Introduction

Molecular dynamics (MD) simulations have provided a wealth of information in recent years about the various aspects of chemistry and physics of water, including the phase transition,^{1–3} the dynamics of hydrogen bonding,^{4–8} the interactions with biological molecules,^{8–17} and the interactions with various surfaces.^{18–22} Curiously, however, little attention has been paid to the simulation of water molecularly dispersed in a glassy polymer network. That is surprising because the *molecular level* interactions between the absorbed water and the polymer network are scientifically challenging, fundamentally and technologically important, and incompletely understood.^{23–28} The consensus of opinion in the polymers community is that the water–network interactions in glassy networks (whether utilized in bulk, adhesives, or composites) hold the key to the prediction of their long-term properties. The quest for understanding those molecular level interactions has motivated the work reported herein and this article marks the first time that a systematic MD simulation of water dynamics and its interactions with a glassy polymer network has been reported.

Simulations were performed on a model epoxy-amine network. The focus here 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 one of convenience. The tendency of epoxy-amine networks to absorb moisture has an adverse effect on their macroscopic (bulk) properties and that has been well-documented.^{29,30} Water–network interactions on the molecular level were also studied experimentally by FTIR,^{31,32} DSC,^{33,34} dielectric relaxation spectroscopy (DRS),^{28,32}

and dynamical mechanical analysis (DMA),^{28,35} yet a number of fundamental questions remain unanswered. Where does the absorbed water reside in the network? In what form (e.g., single molecules, dimers, trimers, etc.)? Do water molecules form hydrogen bonds with the network and, if so, with which groups on the network and in what order of preference? Do water molecules move by translation and/or rotation? And what are the length scales and the time scales (dynamics) of all those events? MD simulation can address those questions but has been hitherto sparsely used.³⁶ The fundamental knowledge gained from the simulation studies, when combined with complementary experiments, is expected to contribute toward the development of a methodology that can predict the degradation of properties and anticipate failure of glassy networks in moist environments.

This article is structured as follows. First we describe the simulation procedure (section 2) and then discuss the destination and location of water molecules within the network (sections 3.1 and 3.2). This is followed by the description of the rotational motion of water (section 3.3). The dynamics of the network polar groups are treated in section 3.4, and the dynamics of various hydrogen bonds (HBs) are described in section 3.5. Finally, we conclude in section 4.

2. Simulation Procedure

MD simulations were conducted with Materials Studio (Accelrys Inc.) software, using the COMPASS force field.³⁷ COMPASS is an ab initio force field that enables accurate and simultaneous prediction of gas-phase properties (structural, conformational, vibrational, etc.) and condensed-phase properties (equation of state, cohesive energies, etc.) for a broad range of

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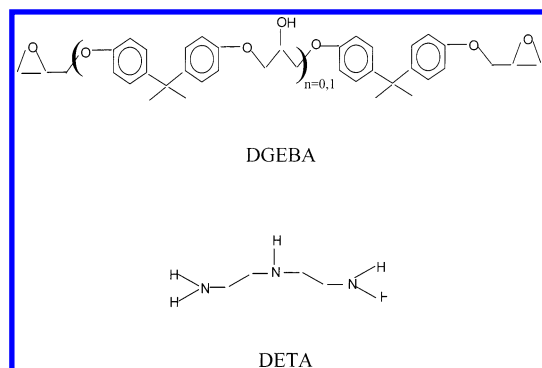


Figure 1. Chemical structure of diglycidyl ether of bisphenol A (DGEBA) and diethylene triamine (DETA).

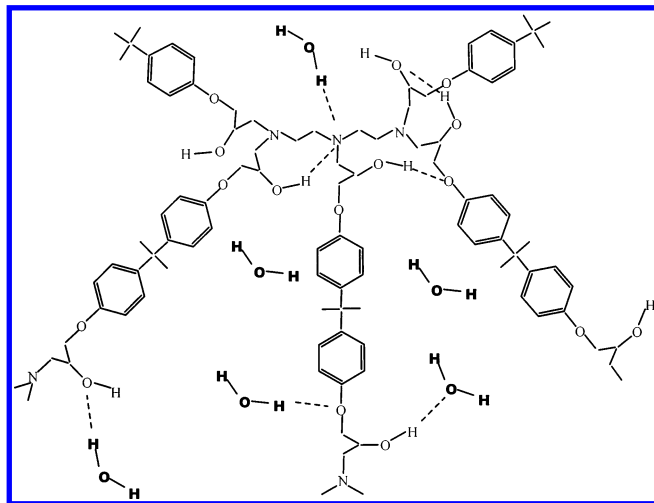


Figure 2. Schematic of a fragment of the chemical structure of the stoichiometric, fully cured water-containing DGEBA-DETA network. Possible HBs between the absorbed water molecules (shown in bold) and/or network groups are denoted by dashed lines.

small molecules and polymers. Simulations were performed on the mixtures of water and a fully cured epoxy-amine network composed of the stoichiometric amounts of diglycidyl ether of bisphenol A (DGEBA) and diethylene triamine (DETA). The chemical structure of the monomers (DGEBA and DETA) is given in Figure 1. A fragment of fully cured network together with a few absorbed water molecules (in bold) is shown in Figure 2. The following simulation procedure was employed. First, a polymer network consisting of 25 molecules of DGEBA and 10 molecules of DETA (the stoichiometric ratio) was built. Next, an amorphous cell was constructed composed of the polymer network and 0–4.75 mol/L (0–8 wt %) of water. The total number of atoms in a cell was about 1400. Each cell was equilibrated for 50 ps followed by a 100-ps MD product run. The length of the product run was determined based on the preliminary simulation (500 ps), which showed that the number of hydrogen bonds between groups (averaged over the simulation time) did not change after the initial 50 ps. Our preliminary simulation also shows that the number of hydrogen bonds between different groups varies among samples. To account for that, we run MD simulation with different initial structures until the number of hydrogen bonds between different groups (averaged over all samples) did not change any more. To meet that requirement, 10 samples were needed for the water content less than 1.27 mol/L (2 wt %) and five samples for higher water content. The cell multipole method (CMM)^{38–40} was used to calculate the long-range Coulomb interactions, and the atom-based summation with 9.5-Å cutoff was used to calculate the dispersion interactions. CMM was chosen rather than the Ewald

method because our preliminary calculation showed that the latter method did not give significantly different result but consumed more (ca. 7 times) computational time. In all simulations, NVT ensembles were utilized with the experimentally obtained density of the dry network equal to 1.165 g/cm³.

3. Results and Discussion

3.1. “Free” Water. In this article the designation “free” water refers to those water molecules that do not form HBs with the polymer network during the 100 ps time frame of our simulations. The following two criteria were used herein to define a hydrogen bond (HB): (1) the distance between hydrogen and an acceptor is less than 2.45 Å and (2) the angle between hydrogen and an acceptor is larger than 145°. Our calculations show that less than 2.5% of the absorbed water is free from HBs with polymer network. This finding is consistent with the experimental results from dielectric relaxation spectroscopy (DRS)³² and nuclear magnetic resonance (NMR)²⁵ and implies that, for the moisture content below 4.75 mol/L (8 wt %), the majority of water molecules remain in close vicinity of the polar groups on the polymer network.

3.2. The Nature of Hydrogen Bonds in Dry and Water-Containing (Moist) Networks. Epoxy-amine networks are replete with polar groups that can engage in hydrogen bonding. We shall therefore start our discussion by examining the nature of hydrogen bonds in the dry network, prior to the onset of moisture uptake. Figure 2 shows a fragment of the chemical structure of a fully cured stoichiometric DGEBA/DETA network. There are three types of polar groups on this network that can participate in hydrogen bonding; hydroxyl groups, ether groups, and tertiary amine groups. The three groups are present in the number ratio of 5:5:3, respectively, and the possible HBs between them are illustrated by dashed lines in Figure 2.

To simplify the description and discussion of our results, an abbreviated notation for each participant (donor and/or acceptor) in a HB and for all hydrogen-bonded pairs was introduced. In our two-letter code, the first letter specifies the hydrogen (or the acceptor) atom that partakes in a HB, while the second letter characterizes the neighboring atom in the parent group. Thus HO represents the hydrogen of the network hydroxyl group, OH the oxygen of the network hydroxyl group, OC the oxygen of the network ether group, and NC the nitrogen of the network tertiary amine. As a special case, Hw and Ow are used to denote water hydrogen and water oxygen, respectively. A hydrogen bond requires two participating atoms, i.e., a pair. In our notation the hydrogen donor group is always listed first and is separated by a hyphen from the acceptor group. For example, HO-OH defines the hydrogen bond between the hydrogen of a network hydroxyl group (HO) and the oxygen of another network hydroxyl group (OH), while HO-Ow defines the hydrogen bond between the hydrogen of a network hydroxyl group (HO) and a water oxygen (Ow). The symbol n_{HB} was used to denote the number of hydrogen bonds. All codes used in the text are summarized in Table 1.

We now focus attention on the simulation of a dry network, where three kinds of HBs are possible (see Figure 2). Each of those three HBs involves hydrogen of the network hydroxyl group (HO) and one of the three acceptors: oxygen of the network hydroxyl group (OH), oxygen of the network ether group (OC), or nitrogen of the network tertiary amine (NC). Our simulation results confirm that all three types of HBs are indeed present. More specifically, of all hydroxyl hydrogens (HO) present in the dry network, about 35% (normalized to the maximum value of 100%) form HBs, while the remaining 65%

TABLE 1: Description of Codes

code	description	atomic electric charge
n_{HB}	number of hydrogen bonds	
HB	hydrogen bond	
HO	hydrogen atom of hydroxyl group on the polymer network	+0.41
Hw	hydrogen atom of water molecule	+0.41
NC	nitrogen atom of tertiary amine group on the polymer network	-0.561
OC	oxygen atom of ether group on the polymer network	-0.202
OH	oxygen atom of hydroxyl group on the polymer network	-0.57
Ow	oxygen atom of water molecule	-0.82
HO-NC	hydrogen bond between HO and NC	
HO-OC	hydrogen bond between HO and OC	
HO-OH	hydrogen bond between HO and OH	
HO-Ow	hydrogen bond between HO and Ow	
Hw-NC	hydrogen bond between Hw and NC	
Hw-OC	hydrogen bond between Hw and OC	
Hw-OH	hydrogen bond between Hw and OH	
Hw-Ow	hydrogen bond between Hw and Ow	

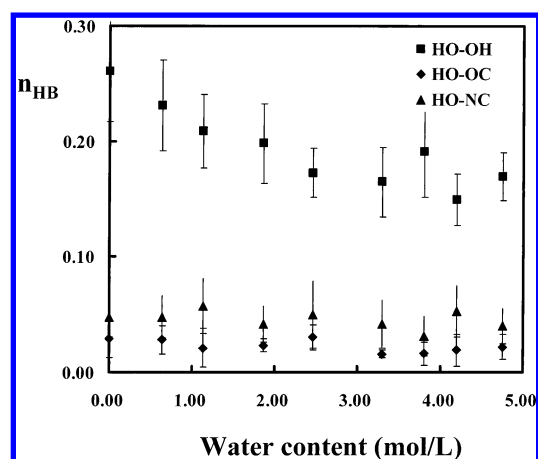


Figure 3. Number of HBs between polar groups of the polymer network as a function of water content. n_{HB} represents an average per hydroxyl hydrogen of the polymer network.

are “free”. The 35% of the HO groups that are engaged in HBs are distributed as follows (see ordinate, Figure 3): 26% form HO-OH pairs, 5% form HO-NC pairs, and 4% form HO-OC pairs.

In a moist environment, water molecules diffuse into the polymer network and engage in hydrogen bonding (see bold entries in Figure 2). We preface the discussion of water–network interactions by stressing that we shall not be principally concerned with the kinetics of moisture absorption. A number of such studies have been reported,^{42–44} but they rarely address the molecular nature of water–network interactions.

We first ask what effect the absorbed water has on the three types of HBs already present in the dry network, namely, HO-OH, HO-OC, and HO-NC? The answer to that question is provided in Figure 3, where the number of HBs (n_{HB}) for each of those three pairs is plotted as a function of moisture content. Note that the n_{HB} for the HO-OH pairs decreases with water uptake initially and then levels off at about 2.5 mol/L (4 wt %) moisture. It is also interesting to note that the water absorbed in this initial stage (between 0 and 2.5 mol/L) breaks up about one-third of the HO-OH HBs present in the dry network. The n_{HB} for the HO-NC and HO-OC pairs does not change appreciably with moisture uptake.

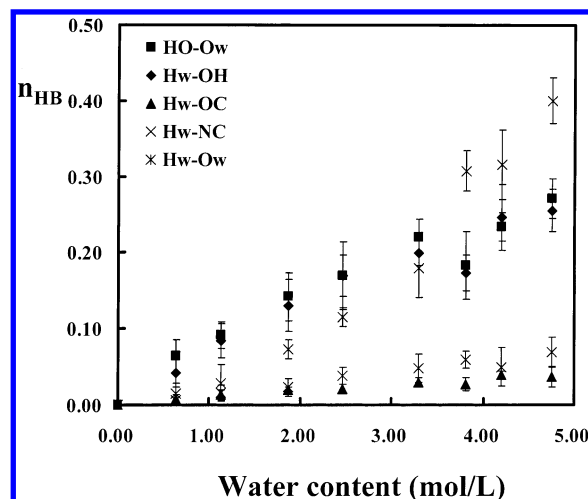


Figure 4. Number of HBs between water and polar groups of the polymer network, and between different water molecules as a function of water content. n_{HB} values are normalized per hydroxyl group of the polymer network.

We now take a closer look at the absorbed water molecules and examine in more detail their destination, their location within the network, and the type of HBs they form. Toward that goal, the number and the type of HBs in which water hydrogen (Hw) and/or water oxygen (Ow) participate was calculated and plotted in Figure 4 as a function of moisture content for five types of HBs. It is apparent that water can form HBs with the network through its oxygen, Ow (e.g., HO-Ow), and/or its hydrogen, Hw (e.g., Hw-OH, Hw-OC and Hw-NC), and/or with other water molecules (Hw-Ow). Up to about 2.5 mol/L (4 wt %) moisture content, the absorbed water shows preference for hydrogen bonding with the network hydroxyl group (HO-Ow and Hw-OH, filled diamonds and squares, respectively, Figure 4). The n_{HB} for the Hw-OH and HO-Ow pairs that form during that time is about the same. The n_{HB} for the Hw-OC and Hw-NC pairs is much smaller and increases slightly with increasing moisture content. At moisture content in excess of 4 mol/L (6 wt %), however, the Hw-Ow HBs become dominant. Nonetheless, when one considers the difference in the concentration between hydroxyl groups of the network and water oxygen (the concentration of the former is 10 times that of the latter at the moisture content of 1%), it becomes evident that the preferential hydrogen bonding sequence of Hw is Ow > OH > NC ~ OC. Figures 4 and 5 also reveal that the absorbed water breaks up some of the HO-OH HBs in the dry network but also forms HBs with the initially “free” hydroxyl groups (65% in the dry network) and, probably, with a fraction of the broken up HO-OH HBs.

Figure 5 is a composite plot of the number of HBs between various network groups, between network and water, and between different water molecules, all plotted as a function of moisture content. All numbers in Figure 5 were normalized with respect to one hydroxyl group of the polymer network, as opposed to one hydroxyl hydrogen in Figure 3. As a consequence, the initial number of HBs in the dry network in Figure 5 is about twice that in Figure 3 (compare the ordinates in Figures 3 and 5 at 0% moisture), because a hydroxyl group can form HBs through its oxygen and its hydrogen. The number of HBs between the network groups decreases with moisture content while the number of HBs between the network and water and between water molecules increases.

Figure 6 shows the n_{HB} computed *per water molecule*. At low moisture content, water forms HBs almost exclusively with

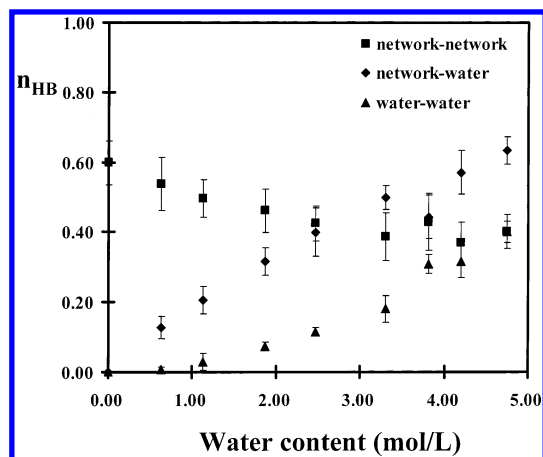


Figure 5. Number of HBs between network polar groups, between water and network polar groups, and between different water molecules as a function of water content. n_{HB} values are normalized per hydroxyl group of the polymer network.

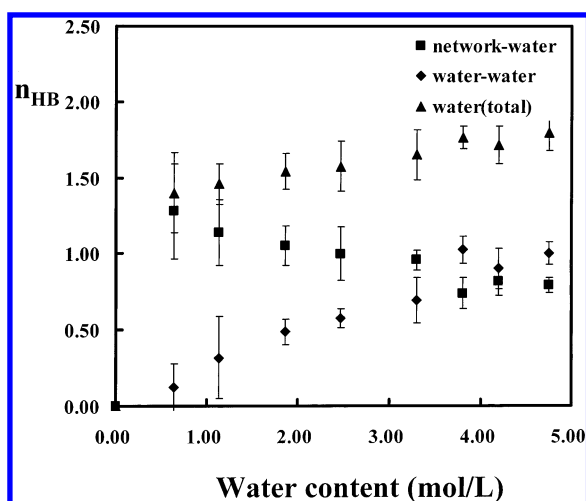


Figure 6. Number of HBs between network polar groups and water and between different water molecules and the total number of HBs of water molecules as a function of water content. n_{HB} values are normalized per water molecule.

the network groups; with an increasing amount of absorbed water, however, a decrease in the number of network–water HBs and a simultaneous increase in the number of water–water HBs is noted. This means that the incoming water molecules are winning the competition with the network groups for the already absorbed water. The total number of HBs per water molecule increases with moisture content; the calculated value of ca. 1.6 at 4 mol/L (6 wt %) moisture content is smaller than the result of our simulation for bulk liquid water of 3.26, which is slightly less than the experimental value of 3.58.⁴⁵

3.3. Rotational Dynamics of Water Molecules. The rotational motion of water molecules was investigated by tracking the three characteristic vectors that correspond to the principal axes of a water molecule, shown in the inset in Figure 7. The vector that connects the two hydrogen atoms is designated HH, the vector directed along the bisector of the H–O–H bend, which coincides with the direction of the water dipole moment, is designated μ , and the vector perpendicular to the plane of a water molecule is designated \perp . The autocorrelation function, $P(t)$, for orientational relaxation of the vectors is given by

$$P(t) = \langle [e(t) \cdot e(0)] \rangle \quad (1)$$

where $e(t)$ and $e(0)$ represent the unit vector (HH, μ , or \perp) at

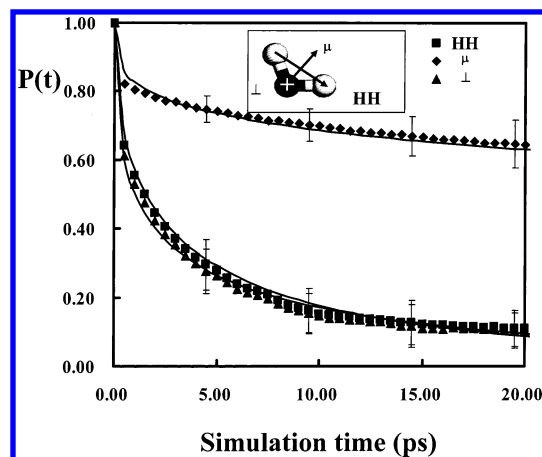


Figure 7. Correlation function (points) of the three characteristic vectors (HH, μ , and \perp). Solid lines are fits to the KWW functional form (eq 2). Water content is 1.27 mol/L (2 wt %).

time t and time 0, respectively, and $\langle \rangle$ denotes the ensemble average over all such vectors and starting times. The time decay of the autocorrelation function to 0.01 is fitted to the Kohlrausch–Williams–Watts (KWW)⁴⁶ two-parameter functional form

$$P_{KWW}(t) = \exp[-(t/\tau)^\beta] \quad (2)$$

where τ is the relaxation time and β the KWW stretch exponent (β_{KWW}). Figure 7 illustrates the time decay of the autocorrelation function for the three principal vectors (HH, μ , and \perp). It is interesting to note that at the end of the 20-ps time interval, vectors HH and \perp have only a 10% recollection of their orientation at time zero, while the vector μ maintains about 60% of its initial orientation. The KWW fits of the autocorrelation function for vectors HH and \perp yielded values of τ_{HH} and τ_{\perp} in the range between 2.5 and 4 ps, independent of the water content. Simulation of bulk liquid water produced the values for τ_{HH} , τ_{\perp} , and τ_{μ} of 2.3, 1.8, and 4.0 ps, respectively, very close to the values reported in the literature (2.8, 2.6, and 1.6 ps for τ_{HH} , τ_{\perp} , and τ_{μ} , respectively).⁴⁷ Our findings suggest that (1) vectors HH and \perp rotate similarly in bulk liquid water and in the water absorbed within the polymer network and (2) the vector μ is slowed considerably through the interactions with the polymer network. Consequently, the rotation of water molecules within the polymer network has anisotropic character.

A slowdown in the orientation dynamics of water has been also observed in the aqueous solutions of proteins,^{8,48} micellae,^{49–52} poly(ethylene oxide),^{53,54} and microemulsions.⁵⁰ The obvious question is what causes this experimentally observed phenomenon? In our case, one possible explanation lies in the confinement imposed by the surrounding network molecules, although such confinement should be isotropic and hence it is not obvious why it would slow one orientational direction more than the others. An alternative explanation could be sought in the ensuing electrostatic interactions and/or hydrogen bonding between the absorbed water and its surroundings. But the electrostatic interactions (Coulomb forces) are weak compared to the hydrogen-bonding interactions,⁵⁵ and hence we believe that hydrogen bonding is the principal mechanism that drives the observed slowdown of the vector μ . To confirm that hypothesis we set out to examine whether (1) the orientation of polar groups with which water forms HBs is at least as slow as the rotation of vector μ and (2) the HBs between water and network groups are sufficiently stable. Those two criteria are addressed in the sections that follow.

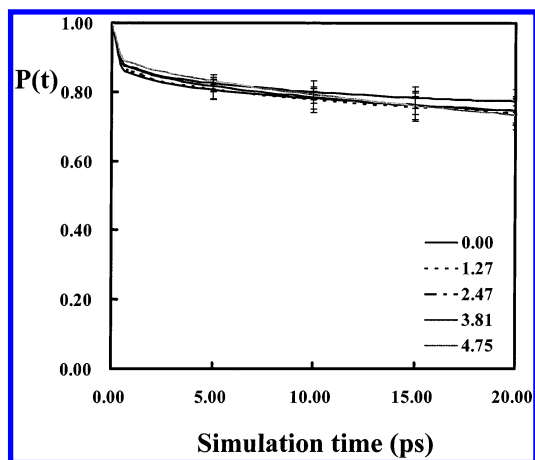


Figure 8. Correlation function of the hydroxyl vector (O–H) as a function of simulation time with water content as a parameter.

3.4. The Orientation of Polar Groups of the Polymer Network. The analysis of the rotational motion of water molecules, described in the previous section, was next extended to the polar groups of the polymer network, namely, the hydroxyl, the ether, and the tertiary amine groups. The analysis was conducted by calculating the autocorrelation function for the following vectors: (1) the H–O vector, connecting the hydroxyl hydrogen with the hydroxyl oxygen, (2) the O–C vector, connecting the ether oxygen with the ether carbon, and (3) the N–C vector, connecting the nitrogen and the neighboring carbon. The autocorrelation function, $P(t)$, for each of those three vectors is of the same form as eq 1. An example of our results is shown in Figure 8, where the change in $P(t)$ for the H–O vector is plotted as a function of simulation time with water content as a parameter. This result shows that the H–O vectors maintain about 75% of their initial orientation after 20 ps. A similar trend was observed for the O–C and N–C vectors, which maintain 90 and 95%, respectively, of their initial orientation after 20 ps. This implies that the polar groups on the network rotate sufficiently slowly to interact with and slow the orientation of water. But to attribute the experimentally observed slowdown in the vector μ to the water–network interactions, one must also show that the ensuing HBs are stable over a required time span, and that is considered next.

3.5. The Dynamics of HB. The lifetime (stability) and the time autocorrelation function of HBs were studied following the rationale put forward by Stillinger.⁵⁶ The average lifetime of a HB, τ_{HB} , defined as the interval between the formation and the breakup of a HB (regardless of its subsequent reformation), was examined first. The calculated values of τ_{HB} are shown as a function of water content for the hydrogen of the network hydroxyl and various acceptors in Figure 9 (HO) and for water hydrogen (Hw) and various acceptors in Figure 10. The lifetime of all HBs is less than 4 ps and the distribution of τ_{HB} shows that more than 85% of HBs are broken in less than 5 ps. A comparison of the lifetimes of the HB pairs that include the hydrogen of the network hydroxyl (Figure 9) yields the following sequence: $\tau_{HB(HO-Ow)} \sim \tau_{HB(HO-OH)} \sim \tau_{HB(HO-NC)} > \tau_{HB(HO-OC)}$. Since the negative charges (set by the COMPASS module and listed in Table 1) of the HB acceptors are Ow (-0.82) < OH (-0.57) \sim NC (-0.561) < OC (-0.202), one would expect $\tau_{HB(HO-Ow)} > \tau_{HB(HO-OH)}$. But that was not borne out by our calculations, implying that water (and hence its oxygen, Ow) can move more rapidly than the hydroxyl groups (OH) of the polymer network. A comparison of Figures 9 and 10 is informative as it reveals that all HBs involving Hw have

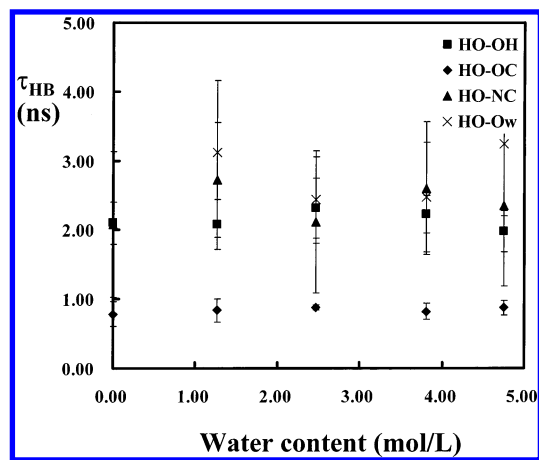


Figure 9. Characteristic lifetime of HBs composed of the hydrogen of the network hydroxyl group (HO) and various acceptors as a function of water content.

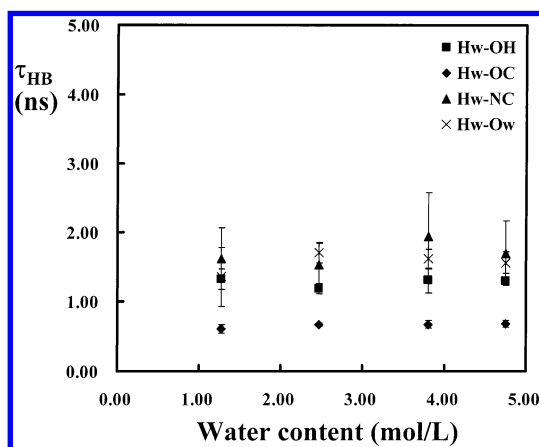


Figure 10. Characteristic lifetime of HBs composed of the water hydrogen (Hw) and various acceptors as a function of water content.

shorter lifetime than HBs involving HO, probably because water can disengage from a HB more easily than the network hydroxyl. The short lifetime of HBs (of the order of several picoseconds) has been observed in a number of systems that include pure liquid water^{5,57} and various aqueous solutions.^{6,11,53} It should be emphasized, however, that the short lifetime of HBs does not imply the separation of water from the network groups because HBs are in the state of continuous formation, breakup, and reformation.

The probability that a randomly chosen HB (i.e., donor–acceptor pair) is bonded at time t , provided that the pair was bonded at time $t = 0$ (independent of the possible breakup and reformation in the interim), is described by the autocorrelation function $C(t)$:⁵⁶

$$C(t) = \langle h(0)h(t) \rangle / \langle h^2 \rangle \quad (3)$$

where $h(t)$ is a binary function for each HB pair $\{i, j\}$ of hydrogen (connected to the HB donor group) and the HB acceptor. Then, $h(t) = 1$ if $\{i, j\}$ are bonded at time t and $h(t) = 0$ if $\{i, j\}$ are not bonded at time t . The symbol $\langle \rangle$ denotes an average over all pairs of $\{i, j\}$ and starting times.

Figures 11 and 12 show the calculated autocorrelation function, $C(t)$, for all possible HB pairs composed of HO and different acceptors (Figure 11) and Hw and different acceptors (Figure 12). The water content in Figures 11 and 12 was fixed at 1.27 mol/L (2 wt %), but analogous results were observed at

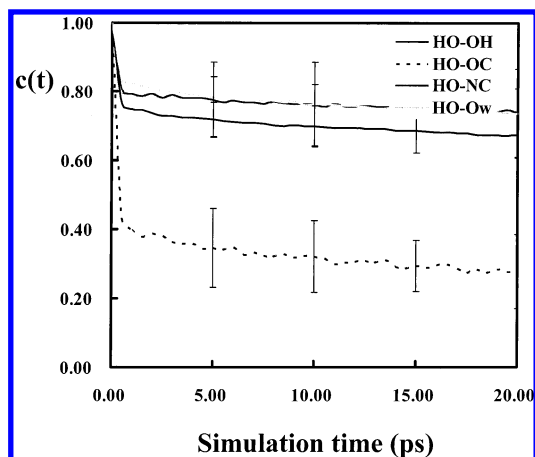


Figure 11. Correlation function, $c(t)$, for HBs composed of the hydrogen of the network hydroxyl group (HO) and various acceptors as a function of simulation time. Water content is 1.27 mol/L (2 wt %).

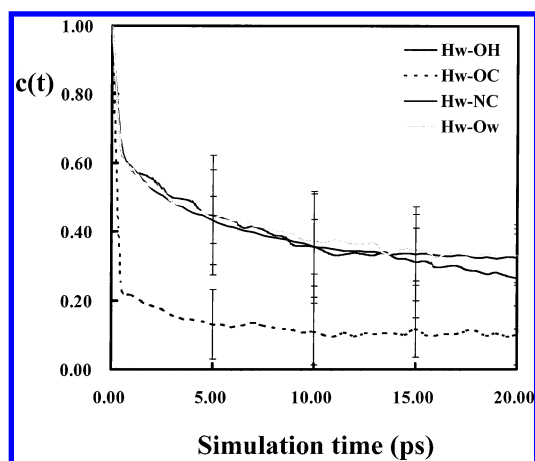


Figure 12. Correlation function, $c(t)$, for HBs composed of the water hydrogen (Hw) and various acceptors as a function of simulation time. Water content is 1.27 mol/L (2 wt %).

other water contents and hence the data in those two figures depict a general trend. From Figure 11 we learn that there exists an 80% probability that hydrogen-bonded pairs HO-OH, HO-NC, and HO-Ow bonded at time zero ($t = 0$) will remain bonded after 20 ps. The probability that a HO-OC pair bonded at time zero will remain bonded after 20 ps is about 30%; the difference is due to the smaller negative charge of OC in comparison with OH, NC, and Ow. Interestingly, the Hw-OH, Hw-NC, and Hw-Ow HB pairs bonded at time zero retain only a 30% probability of remaining bonded after 20 ps, as illustrated in Figure 12. The difference between Figures 11 and 12 could be reconciled by the fact that the translational motion of water is faster than that of the hydroxyl groups. This means that the network groups have higher probability of reforming HBs with previously bonded hydroxyl groups than with previously bonded water.

A quantitative comparison of the dynamics of various HB pairs was made by comparing the characteristic relaxation parameter for each pair, τ_R , defined as $c(\tau_R) = e^{-1}$. The results of our calculations, shown in Table 2, are informative. The key finding is that the characteristic relaxation time for HO-OH, HO-NC, and HO-Ow pairs exceeds 20 ps and hence a longer simulation time is needed for a precise calculation of those values. It is important to reiterate that the results displayed in Table 2 did not change with increasing water content up to 4.75 mol/L (8 wt %) within the simulation time of 100 ps.

TABLE 2: Characteristic Lifetime (τ_R) of Different HBs

HB	τ_R , ps	HB	τ_R , ps
HO-OH	>20	Hw-OH	~10
HO-OC	~20	Hw-OC	~1
HO-NC	>20	Hw-NC	~20
HO-Ow	>20	Hw-Ow	~10

Figure 11 further suggests that the HO-Ow HB is stable enough to slow the orientation of the water dipole in the direction of its dipole moment μ . The complete picture that emerges regarding the rotation of absorbed water can be summed up as follows: the vectors HH and \perp orient freely, much like in the bulk liquid water, while the vector μ , which coincides with the dipole moment, rotates in concert with the hydroxyl groups of the polymer network. Interesting preliminary results were obtained from the longer time MD simulations that are currently under way in our laboratory. The initial findings based on the 10-ns MD runs on the same network with 1.87 mol/L (3 wt %) water were that after 2 ns the network hydroxyl groups and the vectors μ retain 50% and 30%, respectively, of their orientation and that 40% of the original HBs between HO and Ow remain in place. This provides further support for the hypothesis that the vector μ (dipole moment of a water molecule) rotates in concert with the network hydroxyl group. At the same time, this indicates that the relaxation time of the HB(HO-Ow)'s time autocorrelation function is no less than 1 ns. Compared with the MD simulation results of pure liquid water,⁵ where the relaxation time of the HB time autocorrelation function is about 10 ps at 298 K, the relaxation of the hydrogen bonds between water and hydroxyl groups from glass polymers is much slower.

4. Conclusions

We have completed a molecular dynamics simulation study of the interactions and dynamics of water in a fully cured epoxy-amine network with a moisture content of 0–4.75 mol/L (0–8 wt %). The simulations were performed within a 100-ps time frame, and the following principal conclusions were drawn.

Dry epoxy-amine networks are replete with polar groups that can engage in hydrogen bonding. Three types of polar groups on this network participate in hydrogen bonding; hydroxyl groups, ether groups, and tertiary amine groups. The absorbed water breaks up some of the initially present HBs and forms new ones both with the network groups and with other water molecules. The absorbed water forms HBs with the network through its oxygen, Ow (e.g., HO-Ow), and/or its hydrogen, Hw (e.g., Hw-OH, Hw-OC, and Hw-NC), as well as with other water molecules (Hw-Ow). Up to about 2.5 mol/L (4 wt %) moisture content, the absorbed water shows preference for hydrogen bonding with the network hydroxyl group (HO-Ow and Hw-OH.). At the moisture content in excess of 3.8 mol/L (6 wt %); however, the Hw-Ow HBs become dominant. The total number of HBs per water molecule increases with moisture content; the value of ca. 1.6 at 3.8 mol/L (6 wt %) moisture content is much smaller than our simulation result for bulk liquid water of 3.26.

The rotational motion of water molecules was investigated by tracking the three characteristic vectors that correspond to the principal axes of the water molecule. At the end of the 20-ps time interval, the vectors HH and \perp have a 10% recollection of their orientation at time zero, while the vector μ maintains about 50% of its initial orientation. The implication is that water rotates anisotropically; i.e., the rotation of the vector connecting two hydrogen atoms and the vector perpendicular

to the plane of the water molecule is similar to that in the bulk liquid water, while the rotation of the vector coincidental with the dipole moment is much slower. The analysis of the rotational motion of water molecules was extended to the simulation of the orientation dynamics of the three polar groups of the polymer network, namely, hydroxyl groups, ether groups, and tertiary amine groups. The results show that the H-O, O-C, and N-C vectors maintain about 80%, 90%, and 95%, respectively, of their initial orientation after 20 ps.

A quantitative comparison of the dynamics of various HB pairs was made by comparing the characteristic relaxation parameter for each pair, τ_R , defined as $c(\tau_R) = e^{-1}$. The key finding is that the characteristic relaxation time for HO-OH, HO-NC, and HO-Ow pairs exceeds 100 ps. The complete picture that emerges from our study regarding the rotation of absorbed water can be summed up as follows: the vectors HH and \perp orient freely, much like in the bulk liquid water, while the vector μ rotates in concert with the hydroxyl groups of the polymer network.

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