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Spatial Dynamics of Water Molecules Confined in Deuterated Epoxies by Quasi-Elastic Neutron Scattering

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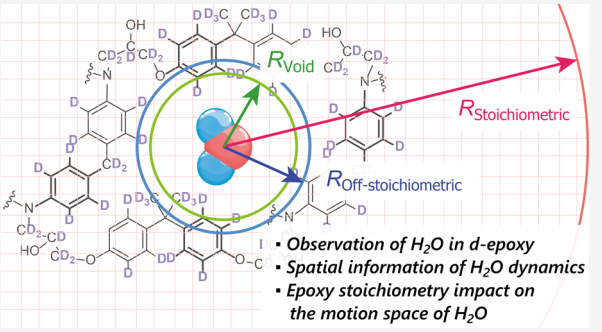
ABSTRACT: The relationship between the water within polymer materials and their material properties is key to expanding their application scope. This study conducted quasi-elastic neutron scattering (QENS) measurements of fully carbon-deuterated epoxies to elucidate the molecular dynamics of water confined in the nanometer-scale voids (nanovoids) of epoxies, focusing on spatial information. The QENS measurements of epoxies with different stoichiometries revealed that the motion space of mobile water molecules in stoichiometric epoxy was more than twice the average size of nanovoids in the epoxy, indicating the broad distribution across multiple nanovoids. In contrast, the extents of oxirane-excess and amine-excess epoxies were close to the nanovoid size. The spatial dynamics of water and its relationship to the chemical structure will help in understanding the water diffusion mechanism and designing epoxy materials with excellent water-related properties, such as water resistance or transport.



INTRODUCTION

The relationship between the water within polymer materials and material properties is key to expanding their application scope. For instance, polymer materials characterized by excellent strength and lightweightedness can address energy challenges in transportation such as vehicles and aircraft; thus, understanding their property changes in wet environments is essential to ensure their reliability. Moreover, the water transport properties are closely related to the water resistance of polymer coatings for electronic devices and the separation performance of reverse osmosis membranes. Epoxy resins are widely used as structural materials, adhesives, and insulating coatings.[1] The amount and rate of water absorption in epoxies determine the water resistance/transport properties. Additionally, water-induced property changes such as swelling,[2,3] glass transition temperature (T_g),[4,5] elastic modulus,[6,7] adhesion,[8,9] and degradation[4] are related to the dynamic behavior of water. Therefore, water dynamics in water-sorbed epoxy continues to be the subject of research because of its importance in basic and applied materials science, such as the performance of epoxy resins, composites, and carbon fiber-reinforced polymers (CFRP) in wet environments.[10−13]

The water molecules in resins consisting of hydrophobic polymers, such as epoxies, are located inside nanovoids in the polymer matrix.[14] The molecular-scale environment significantly impacts water dynamics and is determined by the chemical structure of the polymer. Epoxies are two-component thermosets synthesized from oxirane and amine compounds, which serve as base resins and hardeners, respectively. The chemical structure of an epoxy depends on its stoichiometry, i.e., the ratio of oxirane groups to NH_2 groups. A stoichiometric ratio (oxirane/NH_2 = 2/1) is typical; nevertheless, off-stoichiometric ratios (oxirane/NH_2 ≠ 2/1) are also utilized in practical applications for property modifications. The stoichiometry of an epoxy determines its chemical composition, functional group abundance, and network structure; it also determines the influence of water on the water absorption and physical property changes of the epoxy.[15−17]

The mechanism of water diffusion and its relationship with chemical structures and the changes in material properties remain important challenges that are yet to be fully elucidated. There are numerous studies on the water dynamics in epoxies, including those about the diffusion constant of water and interactions between water and these polymers. It is reported that these dynamics are affected by hydrogen bonds with functional groups in epoxy polymers, particularly oxygen-containing functional groups.[18,19] Infrared (IR) spectroscopy studies indicate that 95% of the water molecules in water-

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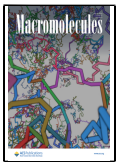

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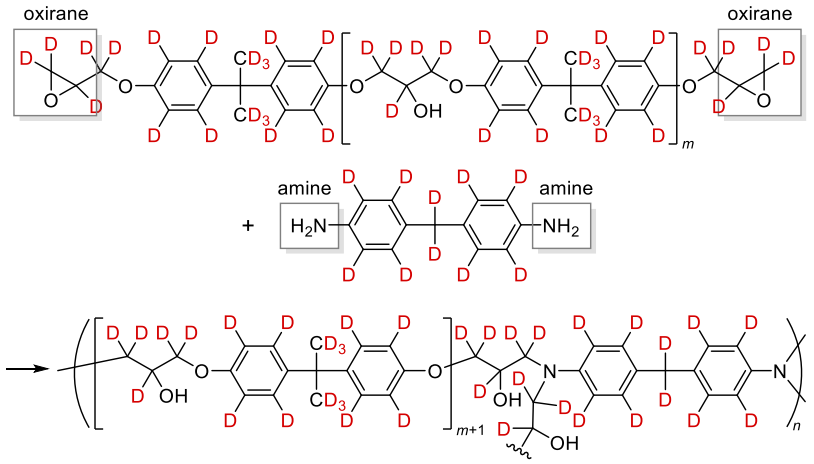

Figure 1. Synthesis of C-deuterated epoxies (bisphenol A repeating unit number: $m \geq 0$). The hydrogen atom at the *ortho*-position of the aniline ring was omitted for clarity owing to its low incorporation ratio.

sorbed epoxies are close to polar functional groups.[20] Solid-state nuclear magnetic resonance (NMR) spectra reveal the existence of two types of water with different relaxation energies: weakly bound and mobile water molecules and strongly bound and immobile water molecules.[21] The fraction of weakly bound and mobile water molecules has been estimated to be 60−80%.[18,22] The diffusion coefficient (D_{eff}) is determined via the weight increase during water absorption using Fick's law.[23] This standard method has been used to elucidate the relationships between D_{eff} and the polymer stoichiometry or chemical structure.[5,16,20,24] The relationship between D_{eff} and nanovoid sizes in epoxies was previously investigated using positron annihilation lifetime spectroscopy (PALS); however, no clear effect of void size was found.[25] On the other hand, the relationship between the free volume of the polymer and water diffusion remains controversial.[26] Some β-relaxation studies indicate that water diffusion is related to polymer chain flexibility;[27,28] however, evidence at the molecular scale is lacking. Recently, molecular dynamics (MD) simulations have been extensively used for the study,[29−31] which showed that water molecules exist in clusters in nanovoids,[32−34] and identified two types of water molecules with different mobilities.[33]

While the above previous investigations on water interactions and D_{eff} provide information about the water dynamics in epoxies, they lack molecular-level spatial information on mobile water molecules. The information is the size of the epoxy polymer involved in water dynamics at a time scale of molecular motion, and it reflects the correlation between the water dynamics and the polymer structure. Since the spatial dynamics of mobile water should play a fundamental role in water diffusion within polymers, quantitatively elucidating this phenomenon is essential for revealing the water diffusion mechanism, controlling the water distribution, and furthermore, manipulating changes in material properties induced by water. D_{eff} should indicate the spatial extent of the water diffusion. However, the D_{eff} determined in conventional water absorption experiments is based on macroscopic observations and is insufficient to explain molecular diffusion and the presence of mobile and immobile water molecules. MD simulations predict the continuous movement of water molecules through nanovoids in epoxy, and the D_{eff} of mobile water determined via this route is 10^1−10^2 times larger than the experimental D_{eff} obtained via the conventional method.[33,34] Thus, more experimental evidence is necessary to understand this phenomenon.

Quasi-elastic neutron scattering (QENS) is the most effective method for experimentally obtaining molecular spatial information on water dynamics because it provides spatial information at the nanometer scale and temporal information at the picosecond scale.[35] Incoherent scattering analysis of the scattering spectrum enables the separation of mobile and immobile water molecules, and QENS measurements can provide the spatial information on mobile water molecules. The water dynamics obtained by observing its hydrogen atoms can be captured separately from the dynamics of polymer chains by deuterating the hydrogen atoms in the polymer because deuterium atoms have a neutron-incoherent scattering cross-section 39 times smaller than that of hydrogen atoms. However, QENS studies on the diffusion of small molecules in deuterated cross-linked polymers are challenging[36] because of the limited availability of such polymers.

In this study, we applied QENS to newly synthesized carbon-deuterated epoxies, in which all hydrogen atoms on the carbon atoms were deuterated to analyze the dynamics of water confined in the epoxy nanovoids (Figure 1). QENS measurements of epoxies with different stoichiometries revealed the diffusivity of water molecules, the ratio of mobile and immobile water, the spatial extent of mobile water dynamics, and their dependence on stoichiometry. The spatial extent of mobile water in stoichiometric epoxy was large, spanning multiple nanovoids, whereas that in off-stoichiometric epoxies was as narrow as a single nanovoid. The results indicated a relationship between the epoxy chemical structure and water dynamics and suggested the contributions of functional groups, the epoxy network structure, and local polymer chain mobility to the observed water dynamics.

EXPERIMENTAL SECTION

Synthesis. C−H bisphenol A diglycidyl ether (BADGE) (h-BADGE) was synthesized from bisphenol A and epichlorohydrin. In contrast, C-deuterated BADGE (d-BADGE) was synthesized from bisphenol A-d_{16} and epichlorohydrin-d_5 treated with NaOH in water. The molar compositions of the monomers and oligomers were determined gravimetrically after fractionation by using preparative gel permeation chromatography (GPC). C−H 4,4′-diaminodiphenylmethane (h-DDM) was synthesized from aniline and formaldehyde, while C-deuterated DDM (d-DDM) was synthesized from aniline-d_7

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and formaldehyde-d_2 treated with HCl in water. Epoxy samples were synthesized by curing a mixture of BADGE and DDM with oxirane/NH_2 molar ratios of 1/1, 2/1, or 3/1 and heating at 180 °C for 3 h. The molar number of oxirane groups in mixtures of BADGE oligomers was calculated from the molecular weight of each component and their composition ratio. The water-sorbed epoxy samples were prepared by immersing the epoxy samples into deionized water at 65 °C until the saturation. The detailed procedures are provided in the Supporting Information.

QENS Measurements. QENS measurements were performed using the BL02 neutron spectrometer at J-PARC MLF.[37,38] This spectrometer has an excellent signal/noise ratio of $>10^5$ and is suitable for collecting the scattering profiles of tiny amounts of water in epoxy. The wavelength of the incident neutron was 6.32 ± 2.07 Å. QENS experiments with an energy resolution of 12 or 3.6 μeV were performed using Si(111) analyzers at 24 °C. The transition energy E (μeV) range was $-0.5 < E < 1.5$ or $-20 < E < 100$, and the scattering vector Q ($4\pi\sin\theta/\lambda$ [Å^{-1}]) range was $0.125 < Q < 1.875$. Plate-cured epoxy samples measuring 20 × 20 × 0.5 mm^3 were wrapped in Nb foil[39] and then sealed into flat cells made of Al alloy (5052). The exposure times for resolutions of 12 and 3.6 μeV were approximately 3 and 7 h, respectively, at a beam power of 530 kW. The $Q-E$ maps of the epoxy samples, empty cells, and vanadium were obtained by subtracting the instrumental background profiles and correcting for detector efficiency by using a vanadium standard. The dynamic structure factor of the samples, $S(Q, E)$, was corrected for detector efficiency by using a vanadium standard. The $S(Q, E)$ of water and epoxy was obtained from Q-slices of the $Q-E$ map at $Q \sim 1$ Å^{-1}.

RESULTS

During the synthesis of d-BADGE, molecules ranging from dimers to oligomers were formed in addition to the target compound because the substrates reacted in a stoichiometric ratio owing to the scalability of the starting materials. GPC analysis of the reaction products confirmed the formation of oligomers with a monomer:dimer:trimer:tetramer:>pentamer molar ratio of 55:33:10:2:2 (Figure S1). The ^{13}C NMR spectrum of d-BADGE (Figure S2) exhibited the characteristics of C-deuterated compounds, including peak splitting by C−D spin coupling and a slight upfield shift of peaks compared with the spectrum of the corresponding h-BADGE. While the ^{1}H NMR spectrum of d-BADGE did not exhibit any signals of the compounds (Figure S3), the spectrum of d-DDM showed a proton signal at the *ortho*-position of the aniline ring with an *o*-H/*o*-D ratio of 16/84, indicating deuterium/proton aromatic substitution during the reaction (Figure S4). The structure of d-DDM was confirmed by ^{13}C NMR; its spectrum exhibited peak splitting and upfield shifts similar to those of d-BADGE and an additional singlet corresponding to the *ortho*-C atom of the aniline ring (Figure S5).

During the synthesis of the epoxies, the mixing ratio of BADGE, including oligomers and DDM, was determined by considering the molar ratio of oxirane and NH_2 groups (Figure 1). In this paper, *epoxy* refers to the sample or a resin material, and *epoxy polymer* refers to the polymer chain or chemical structure of epoxy. In addition to epoxy with an oxirane/NH_2 ratio of 2/1 (**EP2**), epoxies with off-stoichiometric ratios (i.e., amine-excess oxirane/NH_2 = 1/1 [**EP1**] and oxirane-excess oxirane/NH_2 = 3/1 [**EP3**]) were prepared. The C-deuterated epoxies **dEP1**, **dEP2**, and **dEP3** were synthesized from d-BADGE and d-DDM. Similarly, the nondeuterated epoxies **hEP1**, **hEP2**, and **hEP3** were synthesized from h-BADGE and h-DDM. **hEP** was used to characterize the thermal and mechanical properties of the epoxy samples.

Near-infrared (NIR) spectroscopy (Figure S6) of the epoxies confirmed the consumption of oxirane in all samples based on the disappearance of the oxirane signal at 4525 cm^{-1}. In **hEP3** with excess oxirane compared with NH_2, the absence of the oxirane signal was attributed to the ring-opening reaction of oxirane with the OH group. In contrast to the spectra of **hEP2** and **hEP3**, the spectrum of amine-excess **hEP1** clearly exhibited NH_2 and NH signals at approximately 6640 and 5020 cm^{-1}, respectively. The reasonable structures of the epoxy polymers deduced from the functional group analysis described above are shown in Figure 2.

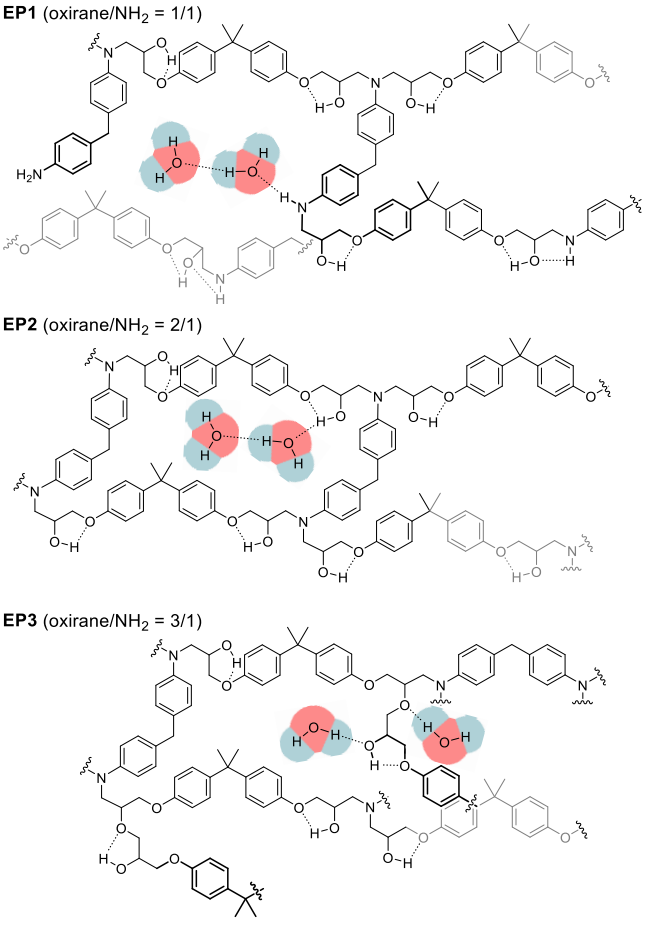

Figure 2. Epoxy polymer structures of (**h** or **d**)**EP** and their estimated interactions with absorbed water molecules. This figure reflects the stoichiometry of oxirane/NH_2 and the reaction of functional groups and shows the number of water molecules based on the maximum absorbed water content. Each structure shows characteristic hydrogen bonds by dotted lines. Hydrogen or deuterium atoms bonded to carbon atoms and the oligomer structure of BADGE are omitted for the sake of clarity. The ratios of BADGE and DDM units are not exact and are indicated for illustration purposes only. Defects in the network structures of **EP2** and **EP3** are not shown.

Differential scanning calorimetry (DSC) measurements showed that **hEP2** and **hEP3** had similar T_g values of 117 and 115 °C, respectively, whereas the T_g of **hEP1** was significantly lower at 84 °C (Figure S7). Dynamic mechanical analysis (DMA) (Figure S8) revealed different peak loss tangent (tan δ) temperatures in the order **hEP1** < **hEP3**< **hEP2**, which agreed with the order of T_g. The temperature ramp profiles of the storage moduli (E') of **hEP2** and **hEP3**

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showed a rubbery plateau at $E' \sim 10$ MPa, giving a cross-linking density of the epoxy polymer network of $\sim 1.0 \times 10^{-3}$ mmol cm^{-3}. The corresponding profile of **hEP1** showed a rubbery plateau with a much smaller E', and the calculated cross-linking density was 0.054 mmol cm^{-3}. The amine-excess stoichiometry in **hEP1** produced a loosely cross-linked epoxy network (Figure 2, **EP1**), which accounted for the low T_g of this sample.[3,12,39,40,41]

The equilibrated water-sorbed epoxies are denoted as (**d** or **h**)**EP+H$_2$O** or **+D$_2$O** and are referred to as *wet epoxies*. The maximum absorbed water content q_{max} of the **hEP+H$_2$O** series was 1.98−2.00 wt % (Table 1), which agrees with previously

Table 1. Summary of the Properties of the (h or d)EP Series

epoxy	EP1	EP2	EP3
composition (oxirane/NH$_2$)	1/1	2/1	3/1
density (g cm^{-3})[a]	1.23	1.19	1.20
cross-linking density (10^{-3} mol cm^{-3})[a,b]	0.054	1.10	0.94
T_g (°C): **EP**[a,c]	84	117	115
T_g (°C): **EP+H$_2$O**[a,c]	64	103	89
q_{max} (wt %)[a,d]	1.98	2.00	2.00
void average radius (R_{PALS}, Å)[a]	2.54	2.58	2.61

[a]Measured using **hEP**. [b]Determined from the modulus in the rubbery region using DMA measurements. [c]Determined by DSC measurements.

reported values.[24,43] These results indicate that only 3% of the total hydrogen atoms in the wet epoxies originated from water molecules in **hEP+H$_2$O** (Table S1). The T_g values of water-sorbed epoxies were 14−26 °C lower than those of the dry epoxies (Figure S7).

The nanovoid sizes of **hEP**, **hEP+H$_2$O**, and **hEP+D$_2$O** were obtained using PALS. Although the epoxy network structure is disordered and the void size and distribution are not uniform, the average void size is anticipated to provide useful information on the spatial scale relationship between the network and water dynamics. The void average radius R_{PALS} of **hEP** with different stoichiometries was nearly identical and slightly increased as the epoxy stoichiometry increased, ranging from 2.54 to 2.61 Å (Table 1, Figure S9). The pore size was not changed by the absorption of H$_2$O or D$_2$O, as indicated by the results for **hEP+H$_2$O** and **hEP+D$_2$O**.

QENS measurements were performed on **dEP+H$_2$O** and **hEP+D$_2$O** to obtain information about the water dynamics in the epoxy polymer and polymer dynamics in the wet state, respectively. Figure S10 shows the $Q-E$ map of **dEP1+H$_2$O**. The measurements illustrated the relationship between Q of the observation space and E. Because Q is the reciprocal of length and time, a smaller Q indicates the dynamic information on a larger space. $E = 0$ indicates elastic scattering with no energy exchange, while $E \neq 0$ indicates quasi-elastic scattering with energy transfer. A large E indicates extensive atom motion because energy corresponds to the inverse of time. **dEP2+H$_2$O** showed both elastic and quasi-elastic scattering, indicating the diffusive motion of water molecules within the epoxy resin (Figure S10). In addition, because the scattering intensity represents the number of hydrogen atoms causing incoherent scattering, the $Q-E$ relationship gives information about the abundance of mobile and immobile hydrogen atoms in water and their dynamics. Even though only a small quantity of water molecules is absorbed in the epoxy, when comparing the incoherent scattering intensity with the amount of H$_2$O corresponding to a fully carbon deuterated epoxy polymer, the scattering intensity of H$_2$O is approximately six times greater than that from the epoxy polymer, showing a significant superiority in the observation.

Figure 3a shows the $S(Q, E)$ profiles of the **dEP+H$_2$O** series, while Figure S11 shows those of **hEP+D$_2$O**. The observed QENS profiles of **hEP+D$_2$O** represent the $S(Q, E)$ of the **hEP** network observing the signals from the hydrogen atoms of the polymer chains. Incoherent scattering from hydrogen atoms from these hydrogen atoms is considerably larger than that from deuterium atoms in D$_2$O because of the smaller scattering cross-section of deuterium than that of hydrogen and the small number of the deuterium atom in **hEP+D$_2$O** (Table S2). However, their dynamics were too slow to be analyzed accurately using the QENS instrument, indicating the immobile nature of the epoxy polymer. By contrast, the QENS profiles of **dEP+H$_2$O** represent the $S(Q, E)$ of H$_2$O and showed the existence of hydrogen atoms with extensive dynamics corresponding to mobile water molecules. Even though we employed C-deuterated epoxies to mitigate the effect of atoms in epoxy polymer and selectively observe the dynamics of H$_2$O in QENS experiments, incoherent scattering from deuterium atoms and polar hydrogen atoms in **dEP** is not negligible (Table S2). However, the dynamics of the epoxy

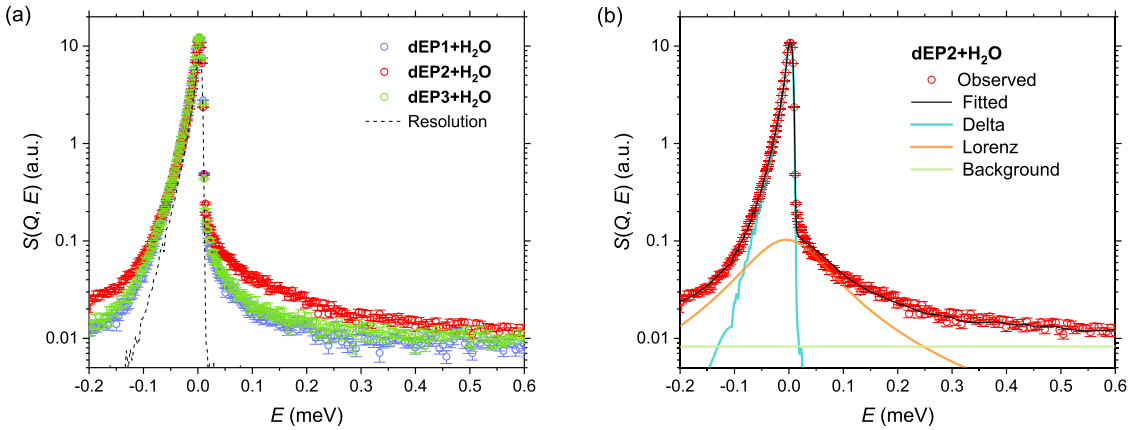

Figure 3. (a) $S(Q, E)$ profiles of the wet **dEP+H$_2$O** series with an average Q of $0.125 < Q < 1.875$. (b) Curve fitting of the $S(Q, E)$ profiles of **dEP2+H$_2$O** with the model represented by eq 1.

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polymer can be analyzed separately from mobile H_2O because it is considered to be nearly immobile. These two sets of $S(Q, E)$ profiles exhibited different scales of water and polymer chain dynamics and indicated that the signals of the remaining hydrogen atoms in **dEP**, hydrogen atoms of −OH and amine (NH and NH_2) groups, and a small number of hydrogen atoms at the *ortho*-position of d-DDM overlapped with those of immobile water in **dEP+H$_2$O**, in contrast to mobile water.

To obtain more detailed information, such as the Q dependence of the samples, we fitted the water dynamics data using eq 1, assuming the existence of mobile and immobile water:[42,43]

$$S(Q, E) = \{A_\delta \delta^{W}(Q, E) + A_L L^{W}(\Gamma, E)\} \otimes R(Q, E) + bg \quad (1)$$

where δ, L, bg, R, and $\otimes$ are the delta function, Lorenz function, constant background, resolution function, and convolution operator, respectively, and A_δ and A_L are the coefficients of the corresponding components. As shown in Figure 3b, eq 1 is suitable for profile fitting (also see the Supporting Information). Figure 4 represents the Q^2 dependence of Γ when $Q^2 < 2.6$ Å^{-2}. The diffusion motion of water molecules in **dEP2+H$_2$O** follows the jump-diffusion model, as shown in eq 2:[35]

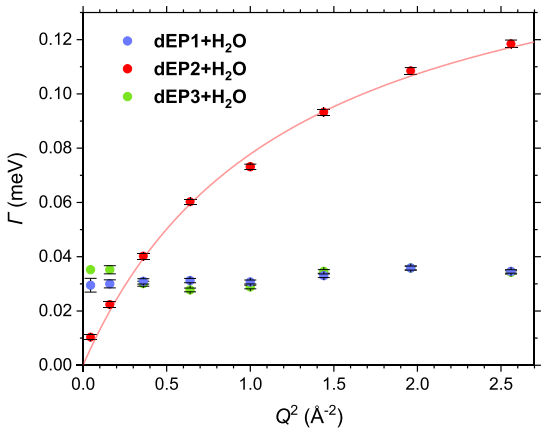

Figure 4. Q^2 dependence of Γ for the **dEP+H$_2$O** series.

$$\Gamma(Q) = \frac{D_{QENS} Q^2}{1 + \tau_0 D_{QENS} Q^2} \quad (2)$$

which gave a diffusion coefficient D_{QENS} of $(2.15 \pm 0.04) \times 10^{-9}$ m^2 s^{-1} and a residence time τ_0 of $(3.80 \pm 0.06) \times 10^{-12}$ s. From the relationship $\langle l \rangle = (6 D_{QENS} \tau_0)^{0.5}$, the jump distance for this diffusion was calculated as 2.21 Å. The D_{QENS} of **dEP2+H$_2$O** is in the same order as the D_{QENS} of bulk water. This indicates that the mobile water in epoxy nanovoids could be categorized as free water, which is only slightly affected by the confinement effect.[44] The D_{QENS} of **dEP2+H$_2$O** is close to those of mobile water in non-cross-linked poly(methyl methacrylate)[45] and poly(ethylene oxide).[46] This observation can be accounted for by considering mobile water as free water. D_{QENS}, in this case, is much larger than the D_{eff} obtained from conventional water absorption experiments using Fick's law at 65 °C ($D_{eff} = 4.13 \times 10^{-12}$ m^2 s^{-1}). These results indicate that D_{QENS} corresponds to the diffusion coefficient of mobile water, whereas D_{eff} is the average diffusion coefficient of mobile and immobile water.

The absence of the Q^2 dependence in **dEP1+H$_2$O** and **dEP3+H$_2$O** suggests local motion, indicating that water molecules within the epoxy network may interact with or be trapped by the epoxy polymer chains.

Because the epoxy network is nearly immobile compared to water molecules as indicated by **hEP+D$_2$O** QENS measurements, the elastic incoherent structure factor of H_2O molecules ($EISF_W$) was estimated according to eq 3, excluding the immobile component in the **dEP** and extracting only the H_2O contribution:

$$EISF_W = \frac{A_\delta - \left\{(A_\delta + A_L)\frac{\sigma_{dEP}}{\sigma_{dEP} + \sigma_{H_2O}}\right\}}{A_\delta - \left\{(A_\delta + A_L)\frac{\sigma_{dEP}}{\sigma_{dEP} + \sigma_{H_2O}}\right\} + A_L} \quad (3)$$

where σ is the cross section of chemical species (Table S2). The $EISF_W$ values calculated for **dEP2+H$_2$O** are almost constant over the entire range of Q. In contrast, those calculated for **dEP1+H$_2$O** and **dEP3+H$_2$O** are larger than those for **dEP2+H$_2$O** and showed an Q dependence (Figure 5). Considering the diameter of the water molecules (2.8 Å),

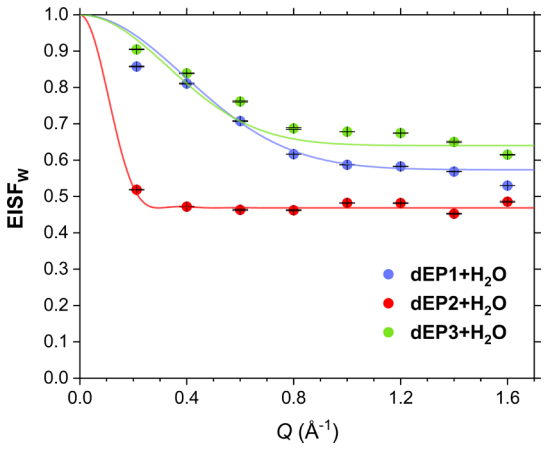

Figure 5. EISF profiles of the **dEP+H$_2$O** series.

the Q scale for molecular motion is approximately 1 Å^{-1}. For **dEP2+H$_2$O**, the equation $EISF_W(Q) = P_m \times (3_{j1}(QR_S)/(QR_S))^2 + 1 - P_m$, where P_m is the ratio of mobile hydrogen atoms ($0 \le P_m \le 1$), R_S is the radius of the space in which mobile hydrogen atoms move, and j_1 is the first-order Bessel function, was used for fitting assuming the dynamics of confined water in a restricted space.[47] For **dEP1+H$_2$O** and **dEP3+H$_2$O**, the equation $EISF_W(Q) = P_m \times \exp(-1/3 \times Q^2 R_B^2) + 1 - P_m$, where R_B is the average amplitude distance of the fluctuations, was employed assuming simple fluctuations.[48−50] The fitting parameters are summarized in Table 2.

Table 2. Fitting Parameters from the EISF Analysis and the Ratio of Mobile Water Molecules[a]

	dEP1+H$_2$O	dEP2+H$_2$O	dEP3+H$_2$O
P_m	0.426 (2×10^{-4})	0.532 (7×10^{-5})	0.360 (3×10^{-4})
R_B (Å)	3.14 (0.002)		3.74 (0.07)
R_S (Å)		15.3 (0.08)	

[a]Standard errors are shown in parentheses.

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R_B (3.14 or 3.74 Å) reflects the radius of the local motion space, which is 4−5 times smaller than R_S (15.3 Å) for **dEP2+H_2O**, indicating the space involved in the time scale of jump-diffusion. The spatial size comparison of R_S and R_B and the average void size R_{PALS} is summarized in Figure 6. The P_m of **dEP2+H_2O** indicates approximately 1.3∼1.5 times as many highly mobile hydrogen atoms, which originates from mobile water molecules, with a relaxation time scale of subnanoseconds compared with that of **dEP1+H_2O** and **dEP3+H_2O**. The remaining hydrogen atoms are less mobile, with relaxation times longer than subnanoseconds, and are represented by the delta function in the $S(Q, E)$ profiles. And thus, P_m indicates the proportion of mobile water molecules within the entire water molecules in epoxy.

The $S(Q,E)$ profiles of the **hEP+D_2O** series were similar to those of all wet epoxies (Figure S11). Because the spectra represent the dynamics of hydrogen atoms in the polymer chains, these results indicate that there are similar polymer chain dynamics regardless of the stoichiometry. In addition, 90−95% of the hydrogen atoms are immobile, which indicate a rigid polymer chain at the experimental temperature below the glass transition temperature. From these results, the ratio of hydrogen atoms with high mobility in **hEP3+D_2O** was calculated as 5.4%, half those in **hEP1+D_2O** and **hEP2+D_2O** (Table S3). This finding implies that stoichiometry determines the fraction of mobile polymer chain segments and that the epoxy chains have a lower flexibility in **hEP3+D_2O** than in other samples.

DISCUSSION

In all epoxy samples examined, the majority of the water molecules exhibited restricted dynamics. On the other hand, the proportion and the spatial extent of mobile water molecules exhibited significant differences of approximately 1.5-fold and 4-fold, respectively, indicating the influence of the epoxy polymer structure and the environment of water molecules on the dynamics (Table 2). The ratios of mobile water molecules in **dEP2+H_2O** were 53%, which is consistent with the reported amount of mobile water,[18,22] whereas they decreased to 43 and 36% in **dEP1+H_2O** and **dEP3+H_2O**. The hydrogen atoms of the mobile water molecules in **dEP1+H_2O** and **dEP3+H_2O** were predominantly associated with local motion over a small motion space, indicating the dynamics of these molecules inside the nanovoids in the epoxy polymer network. By contrast, the mobile water in **dEP2+H_2O** exhibited a large motion space that could be described by the jump-diffusion model, indicating the diffusive nature of these molecules in **dEP2+H_2O**.

The mobile/immobile water molecule ratio depends on the number of hydrogen-bond interactions between the water molecules and the epoxy polymer. The remaining unreacted NH group in **EP1** plays a significant role in hydrogen bonding. The structural feature of **EP3** is the presence of numerous ester cross-links formed via the reaction between −OH groups and oxiranes (Table S4). The phenol ether in the epoxy polymer forms an intramolecular hydrogen bond with the neighboring −OH group. However, the formation of ester cross-links results in the formation of phenol ether without intramolecular hydrogen bonds (Figure 2). The abundance of immobile water in **dEP3+H_2O** suggests that phenol ether has sufficient ability to bind water molecules via hydrogen bonds (Table S4).

The spatial extent of water dynamics in **dEP1+H_2O** and **dEP3+H_2O** analyzed by EISF (Figure 5, R_B = 3.14−3.74 Å) is close to the average void size obtained by PALS (Figure S9, R_{PALS} ∼ 2.6 Å) (Figure 6). Such results support the dynamics

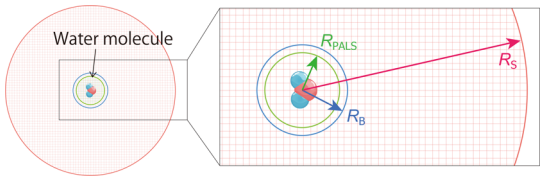

Figure 6. Comparison of the nanovoid radius determined by PALS (R_{PALS} in green) and motion space radius of mobile water molecule determined by QENS (R_S in red and R_B in blue).

of water molecules within a single nanovoid in wet epoxies, as indicated by the Q^2 dependence of Γ (Figure 4). The water dynamics in **dEP2+H_2O** was fitted using the jump-diffusion model with a jump distance of 2.21 Å, plausibly indicating positional translation within a nanovoid. By contrast, the spatial extent of mobile water in **dEP2+H_2O** determined by EISF was R_S = 15.3 Å, more than twice the average void diameter determined by PALS.

Because mobile water molecules are not strongly bound by hydrogen bonds to the polymer chain, the different spatial extents of their dynamics can be ascribed to other structural factors. The voids in polymer resins with nonporous structures are separated by a polymer matrix (i.e., polymer chains). Therefore, the diffusion of small molecules in a void over a large spatial extent is only allowed via the transient interconnection of nanovoids through the dynamic local motion of polymer chains or, in other words, the transient gap of the polymer matrix between nanovoids (Figure 7).[47,48]

QENS analysis of the **hEP+D_2O** series demonstrated that chain motion in the epoxy polymer was more pronounced in **hEP1+D_2O** and **hEP2+D_2O** than in **hEP3+D_2O** (Figure S11). However, considering the existence of numerous non-cross-linked polymer chains in **hEP1**, as evidenced by its low cross-linking density and low T_g (Table 1), the fraction of mobile epoxy polymer chains in **hEP1** may be overestimated. The restricted chain mobility in off-stoichiometric epoxies agrees with the report that the activation energy of β-relaxation is higher for off-stoichiometric epoxies than for stoichiometric ones.[51] Although the reason for this restriction is unclear, it may be related to network-structure characteristics, such as the low cross-linking density and remaining NH groups in **hEP1** and numerous ester cross-links in **hEP3**. Restriction of the chain mobility limits the interconnection of voids and induces the dynamics of mobile water in these voids. By contrast, the larger fraction of the mobile polymer chain in **hEP2** indicates the interconnection of voids, which induces a broad water molecule displacement over multiple nanovoids (Figure 7a−c). The extent of chain mobility observed by QENS and correlated with the motion space of mobile water molecules did not correspond to the degree of segmental chain motion expected from T_g of the epoxies.

The spatial dynamics information provides insights into the relationship among the chemical structure, water diffusion, and property changes induced by water. A recent simulation study posited that the difference between the macroscopic water diffusion in epoxies from the theoretical expectation arises from the heterogeneity of water distribution and diffusivity.[34] Our experiments clearly revealed that the microscopic water diffusion varies depending on the stoichiometry. The

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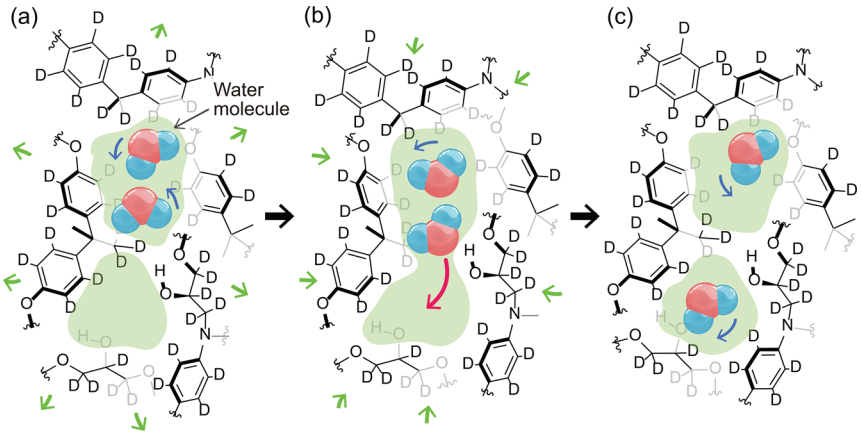

Figure 7. Schematic illustration of plausible water dynamics in relation to epoxy polymer (**dEP**) chain dynamics. The green region indicates nanovoids in the epoxy polymer, the blue and red arrows indicate the motions of water molecules, and the green arrows indicate the motion of polymer chains. (a) and (c) show individual nanovoids separated by the epoxy polymer and (b) shows temporarily interconnected voids owing to the dynamic motion of epoxy polymers. Some deuterium atoms in the epoxy polymer were omitted for clarity.

interrelationship between water dynamics and polymer chain dynamics is possibly one of the factors contributing to the heterogeneity.

Nanoscale water mobility offers proposals for the changes in T_g and other properties of epoxy induced by water absorption. Table 1 shows the effect of stoichiometry and chemical structures on the magnitude of water-induced T_g change in **EP**. The water dynamics in **dEP2+H$_2$O** is characterized by a mobile water ratio that is larger than those of **dEP1+H$_2$O** and **dEP3+H$_2$O** and a broader spatial range than these. Therefore, the stoichiometric epoxy (**EP2**) structure, in which water molecules move in a large space within the time scale of molecular motion, may mitigate the T_g change. In other words, it can be presumed that the epoxy structure with localized water mobility within voids is susceptible to water-induced T_g change. Although there have been reports of T_g and property changes observed in water-sorbed epoxies,[4,5,15,18] there is a lack of systematic studies that take into account the variation in stoichiometry and chemical structure. Such experimental studies would contribute to the evaluation of the proposed model.

CONCLUSIONS

The dynamics of water confined in the nanovoids of **dEP+H$_2$O** epoxies with different stoichiometries were analyzed via QENS measurements. Analysis of the QENS spectra provided quantitative information about the ratio and motion space of highly mobile water molecules. The comparison of QENS spectra of **dEP+H$_2$O** and **hEP+D$_2$O** revealed that the dynamics of water molecules and polymer chains have different time scales. The lower abundance of mobile water molecules in amine-excess **dEP1+H$_2$O** and oxirane-excess **dEP3+H$_2$O** than in stoichiometric **dEP2+H$_2$O** suggested the importance of the amine and phenol ether chemical structures. The motion space of mobile water molecules was much larger in stoichiometric epoxy than in off-stoichiometric ratio epoxies. It was related to the local mobility of the epoxy polymer chain. Consequently, the behavior of water in a single nanovoid is assumed for off-stoichiometric **dEP1+H$_2$O** and **dEP3+H$_2$O** to understand their water dynamics. On the other hand, for stoichiometric **dEP2+H$_2$O**, mobile water molecules move through multiple nanovoids over a time scale of molecular motion; therefore, the water dynamics over a large spatial extent must be considered in conjunction with the local chain motion of epoxy polymers. The insights gained regarding the relationship between the spatial dynamics of water and the epoxy polymer structure are not limited to the series of epoxies with different stoichiometries but can be applied to other epoxies and polymer networks to explain the characteristics of water dynamic behavior. This study can also contribute to the simulation of water dynamics. That is, the experimental information provides guidance for the scale of polymer chain length and interpretation of water dynamic behavior, which helps the understanding of the mechanism. The dynamics information pertains to the mechanisms of diffusion of water within the polymer and their relationship with material properties. These insights would contribute to the future development of high-performance epoxy materials with water suppression, resistance, or transporting properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.3c02010.

Detailed information on the materials, instrumental analysis, synthetic procedures, water absorption experiment, and PALS; GPC, NMR, IR, DSC, DMA, PALS, and QENS experiments; and tables (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) *Chemistry and Technology of Epoxy Resins*; Ellis, B., Ed.; Springer Netherlands: Dordrecht, 1993.
(2) Xiao, G. Z.; Shanahan, M. E. R. Swelling of DGEBA/DDA Epoxy Resin during Hygrothermal Ageing. *Polymer* **1998**, *39*, 3253−3260.
(3) Xiao, G. Z.; Shanahan, M. E. R. Irreversible Effects of Hygrothermal Aging on DGEBA/DDA Epoxy Resin. *J. Appl. Polym. Sci.* **1998**, *69*, 363−369.
(4) DeNève, B.; Shanahan, M. E. R. Water Absorption by an Epoxy Resin and Its Effect on the Mechanical Properties and Infra-Red Spectra. *Polymer* **1993**, *34*, 5099−5105.
(5) Nogueira, P.; Ramírez, C.; Torres, A.; Abad, M. J.; Cano, J.; López, J.; López-Bueno, I.; Barral, L. Effect of Water Sorption on the Structure and Mechanical Properties of an Epoxy Resin System. *J. Appl. Polym. Sci.* **2001**, *80*, 71−80.
(6) Cui, T.; Verberne, P.; Meguid, S. A. Characterization and Atomistic Modeling of the Effect of Water Absorption on the Mechanical Properties of Thermoset Polymers. *Acta Mech* **2018**, *229*, 745−761.
(7) Masoumi, S.; Valipour, H. Effects of Moisture Exposure on the Crosslinked Epoxy System: An Atomistic Study. *Modelling Simul. Mater. Sci. Eng.* **2016**, *24*, No. 035011.
(8) Ogata, S.; Takahashi, Y. Moisture-Induced Reduction of Adhesion Strength between Surface Oxidized Al and Epoxy Resin: Dynamics Simulation with Electronic Structure Calculation. *J. Phys. Chem. C* **2016**, *120*, 13630−13637.
(9) Tam, L.; Lau, D. Moisture Effect on the Mechanical and Interfacial Properties of Epoxy-Bonded Material System: An Atomistic and Experimental Investigation. *Polymer* **2015**, *57*, 132−142.
(10) Vuković, F.; Walsh, T. R. Moisture Ingress at the Molecular Scale in Hygrothermal Aging of Fiber−Epoxy Interfaces. *ACS Appl. Mater. Interfaces* **2020**, *12*, 55278−55289.
(11) Uthaman, A.; Xian, G.; Thomas, S.; Wang, Y.; Zheng, Q.; Liu, X. Durability of an Epoxy Resin and Its Carbon Fiber- Reinforced Polymer Composite upon Immersion in Water, Acidic, and Alkaline Solutions. *Polymers* **2020**, *12*, 614.
(12) Carey, M. S.; Sokol, M.; Palmese, G. R.; Barsoum, M. W. Water Transport and Thermomechanical Properties of $Ti_3C_2T_z$ MXene Epoxy Nanocomposites. *ACS Appl. Mater. Interfaces* **2019**, *11*, 39143−39149.
(13) Lin, K.; Wang, Z. Multiscale Mechanics and Molecular Dynamics Simulations of the Durability of Fiber-Reinforced Polymer Composites. *Commun. Mater.* **2023**, *4*, 66.
(14) Wijmans, J. G.; Baker, R. W. The Solution-Diffusion Model: A Review. *J. Membr. Sci.* **1995**, *107*, 1−21.
(15) Wu, T. H.; Foyet, A.; Kodentsov, A.; van der Ven, L. G. J.; van Benthem, R. A. T. M.; de With, G. Wet Adhesion of Epoxy−Amine Coatings on 2024-T3 Aluminum Alloy. *Mater. Chem. Phys.* **2014**, *145*, 342−349.
(16) Frank, K.; Wiggins, J. Effect of Stoichiometry and Cure Prescription on Fluid Ingress in Epoxy Networks. *J. Appl. Polym. Sci.* **2013**, *130*, 264−276.
(17) Grave, C.; McEwan, I.; Pethrick, R. A. Influence of Stoichiometric Ratio on Water Absorption in Epoxy Resins. *J. Appl. Polym. Sci.* **1998**, *69*, 2369−2376.
(18) Wong, T. C.; Broutman, L. J. Water in Epoxy Resins Part II Diffusion Mechanism. *Polym. Eng. Sci.* **1985**, *25*, 529−534.
(19) Moy, P.; Karasz, F. Epoxy-Water Interactions. *Polym. Eng. Sci.* **1980**, *20*, 315−319.
(20) Mijović, J.; Zhang, H. Local Dynamics and Molecular Origin of Polymer Network−Water Interactions as Studied by Broadband Dielectric Relaxation Spectroscopy, FTIR, and Molecular Simulations. *Macromolecules* **2003**, *36*, 1279−1288.
(21) Zhou, J.; Lucas, J. P. Hygrothermal Effects of Epoxy Resin. Part I: The Nature of Water in Epoxy. *Polymer* **1999**, *40*, 5505−5512.
(22) Diamant, Y.; Marom, G.; Broutman, L. J. The Effect of Network Structure on Moisture Absorption of Epoxy Resins. *J. Appl. Polym. Sci.* **1981**, *26*, 3015−3025.
(23) Lee, M. C.; Peppas, N. A. Water Transport in Epoxy Resins. *Prog. Polym. Sci.* **1993**, *18*, 947−961.
(24) Li, L.; Yu, Y.; Wu, Q.; Zhan, G.; Li, S. Effect of Chemical Structure on the Water Sorption of Amine-Cured Epoxy Resins. *Corros. Sci.* **2009**, *51*, 3000−3006.
(25) Soles, C.; Chang, F. T.; Gidley, D. W.; Yee. Contributions of the Nanovoid Structure to the Kinetics of Moisture Transport in Epoxy Resins. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 776−791.
(26) Kwisnek, L.; Kaushik, M.; Hoyle, C. E.; Nazarenko, S. Free Volume, Transport, and Physical Properties of *n*-Alkyl Derivatized Thiol−Ene Networks: Chain Length Effect. *Macromolecules* **2010**, *43*, 3859−3867.
(27) Soles, C. L.; Yee, A. F. A Discussion of the Molecular Mechanisms of Moisture Transport in Epoxy Resins. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 792−802.
(28) Gerard, J. F.; Galy, J.; Pascault, J. P.; Cukierman, S.; Halary, J. L. Viscoelastic Response of Model Epoxy Networks in the Glass Transition Region. *Polym. Eng. Sci.* **1991**, *31*, 615−621.
(29) Shundo, A.; Yamamoto, S.; Tanaka, K. Network Formation and Physical Properties of Epoxy Resins for Future Practical Applications. *JACS Au* **2022**, *2*, 1522−1542.
(30) Karuth, A.; Alesadi, A.; Vashisth, A.; Xia, W.; Rasulev, B. Reactive Molecular Dynamics Study of Hygrothermal Degradation of Crosslinked Epoxy Polymers. *ACS Appl. Polym. Mater.* **2022**, *4*, 4411−4423.
(31) Guha, R. D.; Idolor, O.; Grace, L. An Atomistic Simulation Study Investigating the Effect of Varying Network Structure and Polarity in a Moisture Contaminated Epoxy Network. *Comput. Mater. Sci.* **2020**, *179*, No. 109683.

(32) Mijović, J.; Zhang, H. Molecular Dynamics Simulation Study of Motions and Interactions of Water in a Polymer Network. *J. Phys. Chem. B* **2004**, *108*, 2557−2563.
(33) Pandiyan, S.; Krajniak, J.; Samaey, G.; Roose, D.; Nies, E. A Molecular Dynamics Study of Water Transport inside an Epoxy Polymer Matrix. *Comput. Mater. Sci.* **2015**, *106*, 29−37.
(34) Yamamoto, S.; Kuwahara, R.; Tanaka, K. Dynamic Behaviour of Water Molecules in Heterogeneous Free Space Formed in an Epoxy Resin. *Soft Matter* **2021**, *17*, 6073−6080.
(35) Bée, M. *Quasielastic Neutron Scattering*; Adam Hilger: Bristol, 1988.
(36) Shudo, Y.; Izumi, A.; Hagita, K.; Yamada, T.; Shibata, K.; Shibayama, M. Diffusion Behavior of Methanol Molecules Confined in Cross-Linked Phenolic Resins Studied Using Neutron Scattering and Molecular Dynamics Simulations. *Macromolecules* **2018**, *51*, 6334−6343.
(37) Kawakita, Y.; Matsuura, M.; Tominaga, T.; Yamada, T.; Tamatsukuri, H.; Nakagawa, H.; Ohuchi, K. Recent Progress on DNA ToF Backscattering Spectrometer in MLF. *J-PARC. EPJ. Web Conf.* **2022**, *272*, No. 02002.
(38) Shibata, K.; Takahashi, N.; Kawakita, Y.; Matsuura, M.; Yamada, T.; Tominaga, T.; Kambara, W.; Kobayashi, M.; Inamura, Y.; Nakatani, T.; Nakajima, K.; Arai, M.; The Performance of TOF near Backscattering Spectrometer DNA in MLF, J-PARC; In *Proceedings of the 2nd International Symposium on Science at J-PARC; JPS Conference Proceedings; Journal of the Physical Society of Japan*, 2015, Vol. *8*.
(39) Tominaga, T.; Sahara, M.; Kawakita, Y.; Nakagawa, H.; Yamada, T. Evaluation of Sample Cell Materials for Aqueous Solutions Used in Quasi-Elastic Neutron Scattering Measurements. *J. Appl. Crystallogr.* **2021**, *54*, 1631−1640.
(40) Hayward, D.; Hollins, E.; Johncock, P.; McEwan, I.; Pethrick, R. A.; Pollock, E. A. The Cure and Diffusion of Water in Halogen Containing Epoxy/Amine Thermosets. *Polymer* **1997**, *38*, 1151−1168.
(41) Vanlandingham, M. R.; Eduljee, R. F.; Gillespie, J. W., Jr. Moisture Diffusion in Epoxy Systems. *J. Appl. Polym. Sci.* **1999**, *71*, 787−798.
(42) Meyer, F.; Sanz, G.; Eceiza, A.; Mondragon, I.; Mijović, J. The Effect of Stoichiometry and Thermal History during Cure on Structure and Properties of Epoxy Networks. *Polymer* **1995**, *36*, 1407−1414.
(43) Popineau, S.; Rondeau-Mouro, C.; Sulpice-Gaillet, C.; Shanahan, M. E. R. Free/Bound Water Absorption in an Epoxy Adhesive. *Polymer* **2005**, *46*, 10733−10740.
(44) Yamada, T.; Takahashi, N.; Tominaga, T.; Takata, S.; Seto, H. Dynamical Behavior of Hydration Water Molecules between Phospholipid Membranes. *J. Phys. Chem. B* **2017**, *121*, 8322−8329.
(45) Fujii, Y.; Tominaga, T.; Murakami, D.; Tanaka, M.; Seto, H. Local Dynamics of the Hydration Water and Poly(Methyl Methacrylate) Chains in PMMA Networks. *Front. Chem.* **2021**, *9*, No. 728738.
(46) Tominaga, T.; Hishida, M.; Murakami, D.; Fujii, Y.; Tanaka, M.; Seto, H. Experimental Evidence of Slow Mode Water in the Vicinity of Poly(Ethylene Oxide) at Physiological Temperature. *J. Phys. Chem. B* **2022**, *126*, 1758−1767.
(47) Mark, T. F.,*A Practical Guide to Quasi-Elastic Neutron Scattering*; Royal Society of Chemistry: Croydon, 2020.
(48) Noferini, D.; Faraone, A.; Rossi, M.; Mamontov, E.; Fratini, E.; Baglioni, P. Disentangling Polymer Network and Hydration Water Dynamics in Polyhydroxyethyl Methacrylate Physical and Chemical Hydrogels. *J. Phys. Chem. C* **2019**, *123*, 19183−19194.
(49) Geise, G. M.; Paul, D. R.; Freeman, B. D. Fundamental Water and Salt Transport Properties of Polymeric Materials. *Prog. Polym. Sci.* **2014**, *39*, 1−42.
(50) Freeman, B. D. Basis of Permeability/Selectivity Tradeoff Relations in Polymeric Gas Separation Membranes. *Macromolecules* **1999**, *32*, 375−380.
(51) Won, Y.; Galy, J.; Gérard, J.-F.; Pascault, J.-P.; Bellenger, V.; Verdu, J. Internal Antiplasticization in Copolymer and Terpolyrner Networks Based on Diepoxides. *Diamines and Monoamines. Polymer* **1990**, *31*, 1787−1792.

https://doi.org/10.1021/acs.macromol.3c02010
Macromolecules 2024, 57, 4254−4262