# Water Transportation in Epoxy Resin

Liang Li,† ShuYong Zhang,‡ YueHui Chen,§ MoJun Liu,† YiFu Ding,† XiaoWen Luo,†
Zong Pu,∥ WeiFang Zhou,∥ and Shanjun Li*,†

*Department of Macromolecular Science, and The Key Laboratory of Molecular Engineering of Polymer, Ministry of Education, Fudan University, Shanghai, 200433, China, School of Chemistry and Environmental Science, Shandong University, Jinan, 250100, China, Department of Macromolecular Material and Engineering, College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, 200065, China and Department of Chemistry, Fudan University, Shanghai, 200433, China*

*Received July 9, 2004. Revised Manuscript Received November 24, 2004*

In the present work, water sorption behaviors at different temperatures ranging from 20 to 80 °C were monitored in a model Novolac cured epoxy resin (EP) and its esterfied ramifications (with $CH_3COO$, $CH_3CH_2CH_2COO$, and $C_6H_5CH_2COO$ side groups referred to as EPA, EPB, and EPP, respectively). In light of gravimetric measurements and positron annihilation lifetime spectroscopy, a sorption mechanism was established, which suggested that the equilibrium water content was thermodynamically controlled, while the diffusion process was kinetically controlled. The driving force of the diffusion resulted in energy released by the hydrogen bonds, whereas the transportation rate was essentially subject to the local-chain mobility as well as the dissociation of water molecules from the epoxy network. To verify this model, dynamic mechanical analysis and time-resolved attenuated total reflection Fourier transform infrared spectroscopy experiments were employed. With generalized two-dimensional correlation analysis, the results obtained from IR spectra were consistent with the mechanism proposed.

## Introduction

The behavior of water diffusion in epoxy networks is a fascinating focus that scientists have been caring about for a long time, for the excellent properties of epoxy materials will be greatly affected by the water absorbed and thus its potential use can be confined.[1]Although mechanical properties of epoxy resins are generally considered to be decreased essentially by a plastisizing effect,[1] the hydrolysis reactions (scission of polymer chains)[2] and water with double hydrogen bonds acting as a physical cross-link[3] can also operate. Nowadays, at least two types of water molecules in the epoxy networks depicted as free/bound water have been generally conceived.[4−19] To obtain a clear picture of the diffusion process, various techniques have been employed in this field, such as near-infrared Fourier transform infrared spectroscopy (NIR−FTIR),[4,5] attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR),[6−8] ultraviolet (UV) reflection,[9] solid-state nuclear magnetic resonunce (NMR),[2,10] dielectric relaxation measurements,[5,11−13] positron annihilation lifetime spectroscopy (PALS),[14−16] electrochemical impendence spectroscopy (EIS),[17,18] fluorescence,[19] and molecular simulations.[5]

Remarkable progress has been achieved owing to a lot of excellent work published.[2−19] However, the information is still far from being well established.

Several models have been put forward to address the issue of the state of water molecules in epoxies. Zhou[3] suggested that there are two types of water molecules with single or double hydrogen bonds to epoxy networks, respectively, while Marechal[20] supposed that water molecules either establish two hydrogen bonds or do not establish any hydrogen bond with their hydrogen atoms. With NIR spectra

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* To whom correspondence should be addressed. E-mail: sjli@fudan.edu.cn. Fax: 86-21-65640293. Tel: 86-21-65642865.
† Department of Macromolecular Science, and The Key Laboratory of Molecular Engineering of Polymer, Ministry of Education, Fudan University.
‡ School of Chemistry and Environmental Science, Shandong University.
§ Department of Macromolecular Material and Engineering, College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science.
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10.1021/cm048884z CCC: $30.25

and molecular simulation,[4,5] however, water molecules with non-hydrogen bond (free water), single hydrogen bond (single bound water), and double hydrogen bonds (double bound water) all can be observed. Although the results obtained by Pethrick,[13] Musto,[4] and Sung[9] seem to be consistent with each other to some extent, when compared with the observations of other authors,[2,5] three essential discrepancies still remain: (I) whether the double bond water molecules have a plasticizing effect or an antiplasticizing effect on the epoxy resins is argued; (II) whether all the water molecules with a typical relaxation time higher than $10^6$ Hz (at room temperature) ought to be attributed to free water is uncertain; (III) whether the hydrogen bonds of single bound waters are formed in self-associated water molecules or along the polymer network is hard to differentiate.

Furthermore, the diffusion process is even confusing. Moy and Karasz[10] suggested that, at low concentrations, water molecules might interact with adjacent bond sites, while at higher concentrations, relatively free water can be observed. In contrast, Adamson[21] concluded that water molecules first occupy free volume holes and then become bound to specific chain segments or groups, and Apicella[22] suggested that the hydrogen bond between polymer hydrophilic group and water takes place after bulk dissolution and moisture absorption onto the surface of vacuoles that define the excess free volume of the glass structure. Besides, in light of previous quadrupole-echo NMR measurements and dielectric measurements,[10−13] the characteristic jumping time of water diffusion process in epoxy networks ($7 \times 10^{-10}$ s) was well consistent with the observation of free water molecules with a relaxation time of $10^9$ Hz, which suggested that the diffusion can be accomplished by free water. While based on important advances following the work of Choppin and Violante in NIR spectra,[23] Musto considered the "jumping" water molecules to be double bound water.[4]

Therefore, no single theory is able to support all sorption phenomena, and water diffusion modes with related mechanisms are still inconclusive and sometimes conflicting.

Recently, the attenuated total reflection Fourier transfer infrared (ATR-FTIR) technique has been developed to provide in situ measurements, by means of which reliable mass−time sorption curves and rich information of the polymer water molecular interactions are available.[24−28] However, the spectrum of water in 3800−3000-cm$^{-1}$ region is superimposed on to a broad absorption band associated with a multiplicity of hydrogen-bonding interactions of OH groups in the polymer network, which complicates the identification. Fortunately, generalized two-dimensional (2D) IR spectroscopy, proposed by Noda,[29−31] is developed to analyze various types of spectral data often obtained under dynamic experiments. This novel method can handle spectral fluctuations as an arbitrary function of time or any other physical variables and is able to probe the specific order of certain events taking place with the development of a controlling physical variable, which is of much significance in the dynamic analysis.[32−35] The technique is now successfully applied to the analysis of ATR spectra. Using 2D correlation analysis on ATR-FTIR spectra, water sorption behavior and the state of water molecules all can be studied as reported by Siesler, Wu, and Li.[6−8,36,37]

In the present study, to monitor the water sorption behavior in a model Novolac cured epoxy resin, its esterfied ramifications were synthesized. Gravimetric measurements were employed accompanied by PALS and DMA, while time-resolved ATR-FTIR spectra were analyzed in terms of generalized 2D correlation analysis. Based on all the phenomena observed, a tentative diffusion mechanism was proposed and three essential problems were discussed: (1) What is the key factor that governs the equilibrium water content? (2**)** What are the driving force and the impeding force of water transportation in epoxy network? (3) How do water molecules diffuse through epoxy network and why is a dual nature presented?

## Experimental Section

**Materials.** *O*-Cresol (2-methylphenol) Novolac epoxy resin (YDCN-702p from Tohto Kasei, Japan, epoxy equivalent, 200−230 g equiv$^{-1}$) and Novolac (H-1, from Sumitomo, Japan, hydroxyl equivalent, 107 g equiv$^{-1}$) were used in this work. The esterified curing agents were synthesized from Novolac (NOV), acetic anhydride, butyric anhydride, and phenylacetyl chloride according to the procedure reported previously. 2-Methylimidazole (2MI, from Wuhan Pharmaceutical Co.) was used as curing accelerator.

**Sample Preparation.** The fresh mixture of epoxy resins, the curing agents and 0.5% of 2-MI was dissolved in A.R. acetone. After solvent was volatized, the specimen was cured in a vacuum oven at 45 °C/15 min, 80 °C/15 min, 120 °C/3 h, 150 °C/2 h, and 180 °C/2 h.

The chemical structures of the cured resins epoxy resins (EP), $CH_3COO$ (EPA), $CH_3CH_2CH_2COO$ (EPB), and $C_6H_5$-$CH_2COO$ (EPP) are shown in Figure 1.

**Gravimetric measurements.** The sample sheets (10 mm × 10 mm × 1 mm) were polished with distilled water and then dried under vacuum oven at 85 °C for a week. Water sorption in the resins as a function of immersion time was monitored by a gravimetric method. The samples were periodically removed from the water, wiped down, and quickly weighed on a Tg332A microbalance (accuracy, 0.01 mg).

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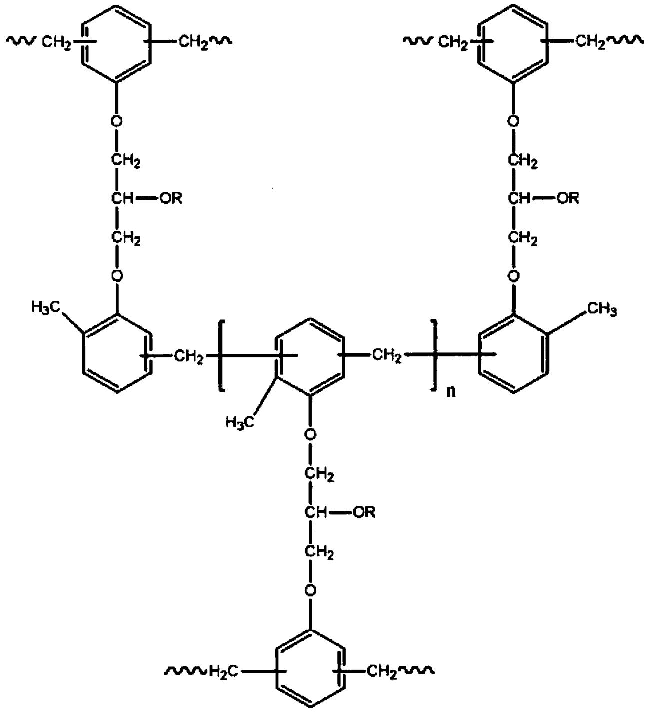

**Figure 1.** Chemical structure of cured epoxy resins: for EP, R = H; for EPA, R = $CH_3CO$; for EPB, R = $CH_3CH_2CH_2CO$; for EPP, R = Ph-$CH_2CO$.

**Positron Annihilation Lifetime Spectroscopy.** Positron annihilation experiments of specimens were conducted on a multichannel analyzer data buffer (Ortec Adcam mode) with a time resolution of 0.27ns full width at half-maximum (fwhm). The probe consists of $BaF_2$ crystal and XP2020Q PMT. About 20 $\mu$g of Ci $Na^{22}Cl$ was directly deposited on one of the samples and then sandwiched between two identical pieces of the samples (12 mm × 12 mm × 1.4 mm). Each spectrum were collected over ~2-h period and consisted of ~$10^6$ integrated counts. The spectra were analyzed using the program PATFIT.

**Dynamic Mechanical Analysis.** The sample sheets (30 mm × 10 mm × 1 mm) were polished with distilled water and then dried under vacuum oven at 90 °C for 1 week. A dynamic mechanical analysis was performed in the dual-cantilever bending mode, using a Netzsch DMA 242 apparatus at a heat rate of 10 °C/min and frequency between 0.1 and 10 Hz.

**Diffusion Measurements by Time-Resolved ATR-FTIR.** All time-resolved ATR-FTIR measurements were performed at 24 °C using a Nicolet Nexus Smart ARK FTIR spectrometer equipped with a DTGS-KBr detector, solid cell accessories, and a ZnSe internal reflection element (IRE) crystal. The spectra were measured at 4-$cm^{-1}$ resolution and 8 scans, and the wavenumber range was 650−4000 $cm^{-1}$. The film-covered IRE crystal with a filter paper above the sample film was mounted in an ATR cell, and the spectra of the dry film were collected as background spectra; then without moving the sample, distilled water was injected into the filter paper while starting the data acquisition by a macro program. A typical sorption loop lasts ~15 min, and acquisition time interval was 27 s. The time-resolved ATR-FTIR spectra in two wavenumber ranges of sorbed water in specimens were obtained from subtraction spectra of the background and the wet sample films.

**Table 1. Diffusion Results Ranging from 20 to 80 °C**

| | EP | | EPA | | EPP | | EPB | |
|---|---|---|---|---|---|---|---|---|
| sample (°C) | $M_\infty$ (%) | $D^a$ | $M_\infty$ (%) | $D^a$ | $M_\infty$ (%) | $D^a$ | $M_\infty$ (%) | $D^a$ |
| 20 | 2.13 | 2.4 | 0.77 | 9.5 | 0.65 | 8.4 | 0.39 | 18.1 |
| 40 | 2.17 | 6.9 | 1.00 | 23.2 | 0.77 | 21.8 | 0.47 | 39.4 |
| 60 | 2.18 | 24.5 | 1.19 | 47.0 | 0.97 | 50.8 | 0.60 | 69.5 |
| 80 | 2.22 | 55.0 | 1.73 | 89.5 | 1.15 | 100.3 | 1.12 | 110.5 |

[a] The unit of diffusion coefficient is $10^{-9}$·$cm^2$·$s^{-1}$.

**Two-Dimensional (2D) Correlation Analysis.** Six spectra at equal time intervals in certain wavenumber ranges were selected for 2D correlation analysis using the software 2D Pocha, which was composed by Daisuke Adachi (Kwansei Gakuin University). Time-averaged reference spectrum was shown at the side and top of the 2D correlation maps for comparison. In the 2D correlation maps, unshaded regions indicate positive correlation intensities, while shaded regions indicate negative correlation intensities.

## Results and Discussion

**Equilibrium Water Content.** *Results of Gravimetric Measurements.* It is generally accepted that the behavior of sorption curves in epoxy can conform to Fickian diffusion, and with reasonable disposals, their diffusion coefficients fulfill the following equation according to Fick's second law.[38]

$$\frac{M}{M_{\max}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right] \quad (1)$$

where $D$ is the diffusion coefficient, $L$ is the thickness of the specimen, and $M_{\max}$ is the equilibrium value of the diffusing water at infinite time.

A simplified form of eq 1 for values of $M/M_{\max}$ lower than 0.6 has the form

$$\frac{M}{M_{\max}} = \left(\frac{4}{L\sqrt{\pi}}\sqrt{D}\right)\sqrt{t} \quad (2)$$

The water sorption (uptake at time $t$, $M_t$) of the sample is achieved as below:

$$M_t = (W_t - W_0)/W_0 \times 100 \quad (3)$$

where $W_0$ is the weight of the dry specimen and $W_t$ is the weight of the wet specimen at time $t$.

Diffusion coefficients ($D$) acquired by curve fitting according to eq 2 and equilibrium water uptake ($M_\infty$) gained from eq 3 are presented in Table 1.

The values of equilibrium water contents follow the order EP > EPA > EPP > EPB in all the temperatures tested. Furthermore, equilibrium water content in EP varies slightly with temperature ranging from 2.13% (20 °C) to 2.22% (80 °C), while for the esterified resins the variations are much more evident.

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**Table 2. Fractional Free Volume Measured by PALS at Room Temperature**

| | $\tau_3$ (ns) | $I_3$ (%) | $R$ (nm) | $Fv$ (%) |
|---|---|---|---|---|
| EP | 1.720 | 20.10 | 0.101 | 7.32 |
| EPA | 1.754 | 20.74 | 0.118 | 9.32 |
| EPB | 1.851 | 21.06 | 0.135 | 14.03 |
| EPP | 1.782 | 20.42 | 0.124 | 10.07 |

Where are these water molecules? Do they just occupy the preexisting free volume?

To answer this question, PALS was employed.

**PALS Results.** We have measured the positron spectra under room temperature, and with the help of PATFIT;[39] three positron lifetimes were resolved for the spectra. The shortest-lived component and the intermediate component are attribution to the self-annihilation of *para*-positronium (*p*-Ps) and the positron annihilation, respectively. The longest-lived component, with lifetime $\tau_3$ and intensity $I_3$, results from the pick-off annihilation of *ortho*-positronium (*o*-**P**s) in the free volume holes. It is assumed that the lifetime $\tau_3$ is proportional to free volume hole size[40] and the intensity $I_3$ is connected with free volume hole number.[41]

Assuming that the free volume holes are spheres, the average radius $R$ of holes and the fractional free volume ($Fv$) were calculated as below:[40,42]

$$\tau_3 = 1/2[1 - R/R_0 + 1/2\pi \sin(2\pi R/R_0)]^{-1} \tag{4}$$

where $R_0$ is the radius of the finite spherical potential, $R = R_0 - \Delta R$ is the radius of free volume, and $\Delta R$ =1.656 Å is an empirical parameter that is obtained by fitting the measured lifetime of cavities with known size.[40,42,43]

$$Fv = 4/3\pi R^3 C I_3 \tag{5}$$

where $C$ is obtained from thermoexpanse results for the system studied here and cannot be used universally.

The results of PALS are listed in Table 2.

Among these systems, the values of free volume have the following order, EPB > EPP > EPA > EP, which seems to be just opposite to the value sequence of the equilibrium water content. Obviously, the fractional free volume cannot be taken as a reliable predictor of the equilibrium water content.

To further investigate this issue, ATR-FTIR experiments were performed.

**2D Correlation Analysis of ATR-FTIR Spectra.** With 2D correlation analysis, the asynchronous correlation spectra were shown in Figure 2; water vibration bands at 3200−3600 cm$^{-1}$ that overlapped in original FTIR spectra were split into two separate bands, $\nu_1$ and $\nu_2$, whose wavenumbers were reported in Table 3.

These two bands indicate that there exists two states of water in epoxy networks,[6−8,36,37] in which one could be confined into relatively free water (at high wavenumbers), while the other could be attributed to bound water (at low wavenumberes) forming a strong hydrogen bond with hydrophilic groups of epoxy networks. This result consistent with the result obtained from solid-state NMR,[10] dielectric measurements,[5,11−13] NIR spectra,[4,5] and UV experiment,[9] which is generally believed.

The equilibrium water content depends not only on the free volume in the matrix (related to relatively free water) but also on how many hydrogen bonds are formed between water and network polar groups (related to bound water). Given that the evidence for the water-induced chain rearrangement is generally provided,[12−16,44] however, these two factors can be related together. For local-scale molecular motions or rearrangement of chain segments is needed to make the polar groups available for water molecules,[14−16] which ought to have influence on the network topology and thus the free volume in which free water is supposed to reside is changed spontaneously. The idea can be partly proved by the fact that, with the increasing water content, the ability of bound water to change the local scale network topology will be limited due to other bound waters around it, which will result in less free water induced by a certain amount of bound water molecules and thus lead to a decrease of free/bound water proportion as observed in NIR measurements,[4,5] UV measurements,[9] and molecular simulation.[5]

Therefore, once the number of polar groups to be bound by water molecules is decided, the extent of how open the matrix is or actual free volume is also determined, followed by certain equilibrium water content.

From the view of thermodynamics, the local-scale motions of small side chains or even rearrangement of chain segments is endothermic ($Q_1$), while forming hydrogen bonds can facilitate the water sorption, which is exothermic ($Q_2$).

The total thermal effect is the combination of $Q_1$ and $Q_2$. So the amount of water absorbed under a given temperature is decided by how strong the hydrogen bond is and how flexible the side chain is. As $Q_1$ is essentially subject to the polarity of network groups, it is reasonable to observe that the equilibrium water content can take a characteristic similar to the sequence of polarity of polar groups as shown below.For EP the highest $Q_2$ can be expected, and increasing the temperature has little influence on the equilibrium water content, which suggests that energy acquired for the whole sorption process can be essentially compensated by hydration interaction. In addition, based on theoretical expectation and a lot of experimental results on the issue of water absorption in polymers with medium to high polarity, Merdas et al. found that the relationship between equilibrium water content and temperature could be well predicted by the heat of dissolution (Hs).[45,46] According to their conclusions, water absorption in polymer systems with the Hs value of 43 kJ

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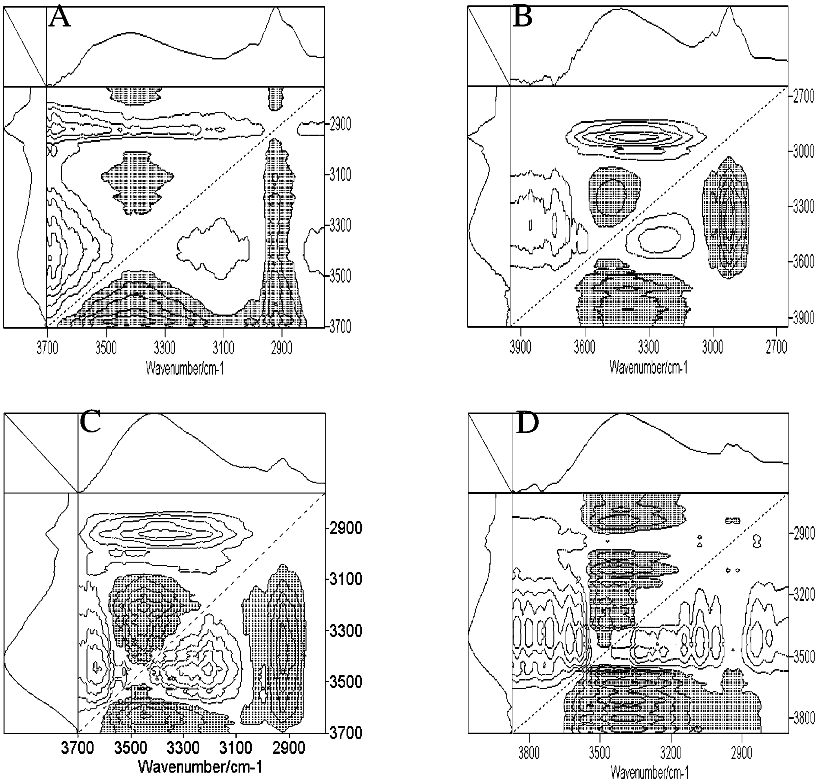

**Figure 2.** Asynchronous 2D correlation spectra of water at 2800−3700 cm$^{-1}$: (A) EP; (B) EPA; (C) EPP; (D) EPB.

**Table 3. Wavenumbers of Separate Bands from Asynchronous Correlation**

| | EP | EPA | EPB | EPP |
|---|---|---|---|---|
| 2800−3700 cm$^{-1}$ | | | | |
| $v_1$ | 3396 | 3480 | 3448 | 3457 |
| $v_2$ | 3129 | 3249 | 3263 | 3272 |

**Table 4. Dielectric Constants of Different Side Groups at 20 °C**

| side group | methanol (in EP) | methyl acetate (in EPA) | methyl butyrate (in EPP) | methyl benzorate (in EPB) |
|---|---|---|---|---|
| dielectric constant | 33.6 | 7.0 | 6.6 | 5.6 |

mol$^{-1}$ will exhibit apparently low dependence on temperature as in the case of EP. While the diffusion activation energy of EP, derived from the Table 1, is 45.2 ± 0.2 kJ mol$^{-1}$, which is a little more than 43 kJ mol$^{-1}$ and can quantitatively qualify the discussion aforementioned.

While for esterfied systems, $Q_2$ provided by a weak hydrogen bond is not large enough for the local-scale motions or even the rearrangement of chain segments, some possible polar sites protected by hydrophobic groups are not accessible for water molecules to interact with at relatively low temperatures. As a result, there is a dramatic increase of absorbed water with the increase of temperature.

**Diffusion Behavior.** Now we come to the question, how do water molecules diffuse through epoxy resins? Do they just go through the preexisting free volume?

As shown in Table 1 at 20 and 40 °C, the order of diffusion coefficients can be presented as EPB > EPA > EPP > EP, while at 60 and 80 °C, it changes to EPB > EPP > EPA > EP. The free volume fraction of these systems, however, is EPB > EPP > EPA > EP at 20 °C, by which a strong relationship is hard to establish. Furthermore, the diffusion coefficients all increase dramatically with the increasing temperature, but an obvious distinction still exists. For esterfied systems, the values of diffusion coefficients increase by a factor of 10, while those of EP increase by a factor of 20 on raising the temperature from 20 to 80 °C. Nevertheless, the difference in the change of free volume between EP and esterfied systems cannot reach such an extent.[47] In addition, the average free volume radius of the systems is in the range of 0.10−0.13 Å, which is a bit smaller than the kinetic radius of a water molecule (∼1.5 Å[8]). Although distribution of free volume inevitably exists and volume with a radius larger than 1.5 Å can be anticipated, it is still hard to imagine that water molecules just diffuse through preexisting free volume.

In light of the above phenomena, generally accepted Frish's theory,[49] and our previous discussion on equilibrium water content, diffusion process may be tentatively described below.

$$\mathrm{H{-}O{-}H} + \mathrm{P_1\,(polar\ group\ 1)} = \mathrm{H{-}O{-}H\cdots P_1}$$
$$(\cdots \text{ represents hydrogen bond})$$

Open a new polar group P$_2$ (polar group 2)

$$\begin{cases}\text{diffusion of water molecular from } \mathrm{P_1} \text{ to } \mathrm{P_2}\\ \mathrm{P_1\cdots H{-}O{-}H\cdots P2}\end{cases}$$
$$(\text{water molecular with double hydrogen bonds})$$

$$\mathrm{H{-}O{-}H} + \mathrm{P_2} = \mathrm{H{-}O{-}H\cdots P_2}$$

According to above mechanism, segment mobility associated with local motions is necessary in order to open

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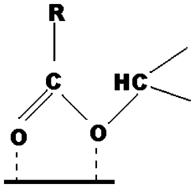

**Figure 3.** Configuration of polar group at the epoxy−metal interface.

**Table 5. Tg Variations of the Studied Systems Obtained by DMA**

| | EP | | EPA | | EPB | | EPP | |
|---|---|---|---|---|---|---|---|---|
| $T$/day | $T_\alpha$ (°C) | $E_a$ (kJ/mol) | $T_\alpha$ (°C) | $E_a$ (kJ/mol) | $T_\alpha$ (°C) | $E_a$ (kJ/mol) | $T_\alpha$ (°C) | $E_a$ (kJ/mol) |
| 0 | 172 | 795 | 139 | 573 | 104 | 453 | 116 | 551 |
| 1 | 161 | 619 | 138 | 560 | 102 | 427 | 114 | 409 |
| 4 | 153 | 466 | 137 | 508 | 101 | 401 | 112 | 391 |
| 7 | 162 | 498 | 135 | 456 | 98 | 394 | 108 | 370 |

additional polar groups, in which at least two factors ought to be considered. For one part, as has discussed before, the average radius of volume holes is less than the kinetic volume of water molecules; thus, a suitable diffusion passage ought to be created before the jumping action. For the other, the ability of polar groups to form hydrogen bonds is limited by certain configurations, i.e., the hydrophilic oxygen atom in the polar group can be protected from interacting with water molecules by hydrophobic methyl or methylene. Take EPA, for example, the acetoxy groups immediately adjacent to the epoxy−metal surface ought to turn their oxygen atoms toward the metal surface with hydrophobic methyl groups pointing out as shown in Figure 3. The well-arranged layer formed by these special conformations can thus be difficult to reshap, and protect the polar atoms beneath from being bound by water molecules, which results in the water concentration on the interface to be fairly lower than that in bulk resins as we reported before.[17,18]

Therefore, specific configurational changes prior to the jumping process are necessary.

In general, on condition that macrocracks are not formed, water molecules will jump from one polar site to another and leave the origin site open for another water molecule to occupy. The jumping action is accomplished either by water molecules without hydrogen bond (free water) or by water molecules with double hydrogen bonds (double bound water), which depends essentially on the distance between two polar groups. During the process, the topology of the epoxy network is changed due to local-scale segmental motions, followed by the change of population of relatively free water molecules. The driving force of the diffusion results in the energy released by new hydrogen bonds. While the impeding step of diffusion origins from not only the local rearrangement of chains to open the additional polar sites but also energy needed for water molecules to dissociate from epoxy networks (dehydration). As the hydration process is quick to establish, the transportation rate of water is kinetically controlled by the local-chain mobility as well as dehydration.

To verify the assumption proposed, generalized 2D correlation analysis has been employed, which is able to probe the specific order of certain events taking place in the system and has been successfully applied in the field of water diffusion process in different polymers. According to the rule of Noda,[29−31] the sign of asynchronous correlation peak $\Psi$ ($\nu_1$, $\nu_2$) gives information about the sequential order of intensity changes between band $\nu_1$ and band $\nu_2$. If the sign of the asynchronous band $\Psi$ ($\nu_1$, $\nu_2$) is positive (unshaded area), band $\nu_1$ varies prior to band $\nu_2$, while the negative asynchronous band (shaded area) implies the opposite phenomena. Take Figure 2A, for example; the negative band $\Psi$ (3396, 3129) reveals that the change of the population of the strong hydrogen-bonded OH species (3129 cm$^{-1}$) occurs earlier than the change of the population of the weak hydrogen-bonded OH species (3396 cm$^{-1}$). Similarly, in all the systems studied here (as shown in Table 3), the strong hydrogen bound water molecules (presented at 3129, 3249, 3263, and 3272 cm$^{-1}$ for EP, EPA, EPB, and EPP, respectively) are all produced prior to the relatively free ones (presented at 3396, 3480, 3448, and 3457 cm$^{-1}$ for EP, EPA, EPB, and EPP, respectively). Thus, the conclusion can be drawn that the strong hydrogen bond which is energetic favorable appears earlier in the water diffusion process, which is consistent with the assumption that relatively free water molecules are induced resulting from the jumping process of bound water.

In addition, absorbed water molecules forming double hydrogen bonds will cause an increase of Tg, which has been found in other epoxy resins.[3] And from DMA results, we do observe an increase of Tg after 7-days absorption in EP, which partly supports the assumption above.It should be noticed that the change of Tg depends not only on the double bound water molecules but also on the plastizing effect. So the results here do not indicate that only after a long period of sorption can water molecules form double hydrogen bonds. On the contrary, in the initial stage of sorption experiments, water molecules with double hydrogen bonds were generally observed in different epoxy systems.[4,5]

As far as EP is concerned, the thermal energy needed for the whole water absorption process is fairly small due to the energy released by lots of strong hydrogen bonds, while diffusion related to the dehydration can be readily accelerated on raising the temperature. Thus, its equilibrium water content is thermoinsensitive, while its diffusion coefficient is strongly thermodependent. Another point worth emphasizing is that, when the rate of dehydration is enhanced with increasing temperature, more water molecules can be absorbed initially, followed by more hydrogen bonds and energy released. As a result, the diffusion process in EP at high temperature can share some characteristic of a self-accelerating process, which makes its relative increment (the value increased compare to its origin value at low temperature) of diffusion coefficient much higher than those of esterfied ones. The same process may generally exist, but it is relatively unremarkable in esterfied systems due to mild hydrogen bonds and less energy released. However, the absolute value of diffusion coefficient in EP is still much lower than those of esterfied systems at any given temperature due to its strong water−epoxy interaction.

## Conclusion

In the present work, water sorption behaviors in a model Novolac cured epoxy resin and its esterfied ramifications were monitored. The results of gravimetric measurements clearly demonstrated that the equilibrium water content of EP was thermoinsensitive, while its diffusion coefficient was strongly thermodependent. In esterfied systems, however, these two parameters all increased greatly on raising the temperature. The difference observed here cannot be explained according to the contribution of preexisting free volume as investigated by PALS measurements, which was consistence with recent studies as reported by other authors. In addition, time-resolved ATR-FTIR spectra were analyzed in terms of generalized 2D correlation analysis, from which two remarkable conclusions could be drawn: (I) There are two kinds of water molecules existing in studied cases, in which one could be confined into relatively free water (at high wavenumbers), while the other could be attributed to bound water (at low wavenumberes) forming a strong hydrogen bond with hydrophilic groups of epoxy networks. (II) The strong hydrogen-bonding water molecules are produced prior to the relatively free ones. Based on the above phenomena and observations of other authors, a tentative sorption mechanism was established, which indicated that the equilibrium water content was thermodynamic controlled, while the diffusion process was kinetic controlled. The driving force of the diffusion resulted in the energy released by the hydrogen bonds, whereas the transportation rate was essentially subject to the local-chain mobility as well as the dissociation of water molecules from the epoxy network.

CM048884Z