Effect of curing conversion on the water sorption, corrosion resistance and thermo-mechanical properties of epoxy resin

Huiping Wang, Yi Liu, Jie Zhang, Tian Li, Zhongnan Hu and Yingfeng Yu*

The study of the relationship between curing conversion and the properties of the material is critical for optimizing the performance of epoxy materials. In this article, the change in the thermo-mechanical and corrosion resistance properties of the diglycidyl ether of a bisphenol A/diaminodiphenylsulfone epoxy system with curing conversion was studied using various instruments. The water sorption process showed the opposite trend of equilibrium water content with curing conversion at high and low temperatures, which was found to be related to different mechanisms by infrared spectroscopic study. The mechanical tests and corrosion resistance (EIS) experiments showed an optimized performance region at a curing conversion close to ca. 85%.

1. Introduction

With the rapid development of the aerospace and microelectronics technologies, epoxy resins as structural and packaging materials are required to possess an even better performance ever before. In addition the research of novel high performance epoxy systems, optimization of the properties of existing epoxy materials through processing and structure–property studies is another effective route to improve the performance of materials.

In previous works,1–4 the thermo-mechanical properties of epoxy resin with different curing conversions were carefully studied; however, most of the results are somehow inconsistent with each other.5–8 However, there are only a few reports on the relationship between corrosion resistance and curing conversion.

With various polar groups, such as hydroxyl and amino groups, epoxy resins are vulnerable to absorbing water, thus leading to a catastrophic effect on their properties such as mechanical properties and corrosion resistance. Water molecules could be transported to the resin matrix and metal–resin interface and lead to performance loss when epoxy resin is used as coating or adhesive in various application fields.

For epoxy coatings, Shreepathi et al.9 found that the equilibrium water content was an important factor of corrosion resistance, coatings with a lower equilibrium water content showed better corrosion resistance through electrochemical impedance spectroscopy (EIS) and salt spray exposure tests. Kamisho et al.10 obtained a similar result and suggested that the equilibrium water content affected adhesive performance considerably more than the diffusion coefficient. Liu et al.11 further demonstrated that increasing the crosslink density could improve the corrosion resistance of coatings. A clear, understanding of the water sorption mechanism is crucial for the corrosion resistance of epoxy resins.

Water molecules that diffuse in the epoxy network may act as diluents, and thus lead to a loss in its properties.12 However, Macqueen et al.13 found that the free volume of an epoxy resin decreased after water sorption, which may result from the anti-plasticizing effect of the water molecules occupying the original free volume of the epoxy resin. However, Choi et al.14 observed that the $T_g$ increased after water sorption due to the additional curing of epoxy during this process.

To organize the contradictory results above, the hydrogen bond theory was applied to explain the interaction between epoxy and water molecules.15–21 Three types of water molecules may exist depending on their interactions with epoxy: without hydrogen bonds ($S_0$); with one hydrogen bond ($S_1$); and with double hydrogen bonds ($S_2$). $S_0$ and $S_1$ water molecules work as a plasticizer, and $S_2$ works as an anti-plasticizer. Two-dimensional (2D) ATR-FTIR spectroscopy was further combined22–26 with the hydrogen bond theory for the study of water diffusion in epoxy resins at low temperatures.

In our previous works,27–29 we found that polarity and free volume are the most important factors which influence water sorption in epoxy resins. Polarity is the primary factor determining the equilibrium water content, while free volume mainly affects the diffusion coefficient. As for the water sorption with different curing conversions, Nogueira et al.12 found that epoxy resins with higher conversion have a larger equilibrium water content at low temperatures to give a highly polar structure. However, the result from Enns et al.29 shows that the equilibrium water content of epoxy resins increased with the
increasing curing conversion at room temperature due to more free volume. Frank et al. obtained a similar result. However, few research have systematically studied the effect of curing conversion on the properties of epoxy resins, and the corrosion resistance with water diffuse behaviour at both high and low temperatures.

In this work, we selected one of the most well-used epoxy systems, the diglycidyl ether of bisphenol A/diaminodiphenyl-sulfone (DGEBA/DDS), as the model to study the relationship between curing conversion and thermo-mechanical, water sorption, and corrosion resistance properties. The results would be helpful for understanding the corrosion resistance performance and property changes of epoxy materials with the curing procedure.

2. Experimental

2.1 Material

Diglycidyl ether of bisphenol A epoxy resin (DGEBA) (DER 331, Dow chemical Co. epoxy value, 0.51–0.55 mol/100 g epoxy), and the curing agent 4,4’-diamino-diphenylsulfone (DDS) was manufactured by the Sinopharm Chemical Reagent Co. (Shanghai, China). The chemical structures of DGEBA and DDS are illustrated in Scheme 1.

**Specimen preparation.** Samples were prepared by dissolving the curing agents in epoxy resins in a stoichiometric epoxy/amine molar ratio at 150 °C, and then curing for different times as shown in Table 1, in which the curing conversions were monitored by near-IR with a deviation of ca. 2%. The curing procedures with different curing conversions were performed on the basis of the iso-thermal DSC study.

2.2 Experimental techniques

**Different Scanning Calorimetry (DSC).** Calorimetric analyses were carried out on a Mettler DSC-823e thermal analyzer. Samples of approximately 5 mg in weight were cured in aluminium pans in a nitrogen atmosphere. In the isothermal and dynamic curing process, the degree of conversion by DSC was calculated as follows:

\[ \alpha_{DSC} = \frac{\Delta H_f}{\Delta H_{total}} \]  

where \( \Delta H_f \) is the heat released up to the temperature \( T \), which is obtained by the integration of the calorimetric signal up to this temperature in the dynamic process, while for isothermal curing it corresponds to a curing time \( t \), and \( \Delta H_{total} \) is the total reaction heat associated with the complete conversion of all reactive groups.

**Dynamic Mechanical Analysis (DMA).** The dynamic mechanical properties were collected with a Netzsch DMA 242 operating in the double cantilever mode at an oscillation frequency of 1 Hz. The specimens for DMA were prepared in the form of cuboid bars with the nominal dimensions of 30 × 10 × 1 mm. The data were collected from 50 °C to 250 °C at a scanning rate of 3 °C min \(^{-1} \).

**Mechanical test.** The Izod impact test was performed at room temperature (RT) using an Izod 5110 impact tester, according to ISO 180–2000 using unnotched rectangular specimens. The pendulum employed had a kinetic energy of 1 J. The impact strength was obtained by taking the average values of ten specimens.

The T-peel adhesion strength between copper foil and epoxy composites were using an Instron Model 5565 universal tester according to the IPC-650-650 standard at RT. Each test reported is the average of at least five sample measurements.

**Gravimetric measurements.** The sample sheets (10 mm × 10 mm × 1 mm) were polished with distilled water, and then dried in a vacuum oven at 100 °C for 24 h. Water sorption at 35 °C and 75 °C was then monitored in the resins as a function of immersion time. The samples were periodically removed from the water, wiped down and quickly weighed on a Tg332A microbalance (accuracy, 0.01 mg). The water sorption (content at time \( t \), \( M_t \)) of the sample is achieved as below:

\[ M_t = \frac{W_t - W_0}{W_0} \times 100\% \]  

where \( W_0 \) is the weight of the dry specimen, and \( W_t \) is the weight of the wet specimen at time \( t \).

**Diffusion measurements by time-resolved ATR-FTIR.** All time-resolved ATR-FTIR measurements were performed at 35 °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 32 scans, in the wavenumber range 2700–3700 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. Next, without moving the sample, distilled water was dropped on the filter paper while starting the data acquisition by a macro program. The thickness of the films was about 15 mm.

**Diffusion measurements by near-IR.** Samples with different curing conversions were immersed in distilled water at 75 °C, and near-IR transmission spectra were recorded at selected time intervals during the immersion. The near-IR spectra, at 4 cm \(^{-1} \) resolution and 128 scans, were then obtained using a Nicolet Nexus 470 with a white light source and an MCT detector. The thickness of the samples was about 5 mm.

**Two dimensional (2D) correlation analysis.** A series of spectra at equal time intervals in certain wavenumber ranges was selected for a 2D correlation analysis using the 2D Shige software. The time-averaged reference spectrum is shown at the
side and the top of the 2D correlation maps for comparison. In the 2D correlation maps, the red regions indicate positive correlation intensities, while the blue regions indicate negative correlation intensities.

**Electrochemical impedance spectroscopy (EIS) measurements.** EIS measurements for the epoxy-coated metal systems were performed on a CH650E electrochemical workstation (Shanghai Chenhua Instruments Inc., China) in 3.5 wt% NaCl solution using a three-electrode system. An epoxy-coated stainless steel acts as the working electrode; the thickness of the coatings was about 100 μm; a saturated calomel electrode (SCE) was used as the reference electrode and platinum sheet electrode (15 × 15 mm) was used as the counter electrode. The coating area exposed to the electrolytic solution was 1.7671 cm² (R = 1.5 cm). All the measurements were carried out at an open circuit voltage by applying a sinusoidal voltage of 5 mV and the spectra were recorded in the frequency range of 0.1 Hz to 1000 kHz.

### 3. Results and discussion

#### 3.1 Effect of curing conversion on the thermo-mechanical properties

An increase curing conversion enhances the thermal transitions of epoxy resins such as the glass transition temperature ($T_g$) due to the change of the crosslink density and free volume. $T_g$ as a function of conversion, which was reported by many authors.\(^2\)\(^3\)\(^2\) DMA is a powerful method for the characterization of the relationship of $T_g$ and curing conversion.\(^1\)\(^1\)\(^3\)

Fig. 1 shows the DMA study of the DGEBA–DDS system with different curing conversions. Both the storage modulus and $\tan \delta$ increased as the curing conversion increased, and the enlargement of the storage modulus after the $T_g$ transition suggests the increased crosslink density. In this study, the peak temperature of $\tan \delta$ is defined as the glass transition temperature. The $T_g$ versus conversion data is shown in Fig. 1c, in the low conversion region, $T_g$ versus conversion exhibits an approximate linear relationship due to the chain-end concentration decrease, but $T_g$ sharply increased in the high conversion region as a result from the combination of the chain-end concentration decrease and crosslink density increase.\(^2\)\(^) This $T_g$-conversion relationship is consistent with other reports on epoxy resins.\(^2\)\(^3\) The $T_g$-conversion relationship has been studied in numerous works,\(^2\)\(^3\)\(^4\)\(^5\) and the DiBenedetto equation is well accepted:

$$\frac{T_g - T_{\theta0}}{T_{g0} - T_{\theta0}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha}$$

where $\alpha$ is the curing conversion, $T_{\theta0}$ is the $T_g$ of the unreacted monomers mixture, $T_{g0}$ is the $T_g$ of fully the cured thermoset, $\lambda$ is the $\Delta C_p$ values of the fully cured and unreacted materials.

By fitting the experimental data into eqn (3), which is shown as a red line in Fig. 1c, it can be found that the equation can well describe the $T_g$-conversion relationship with a square error of $R^2 = 0.995$.

![Fig. 1](image_url)

**Table 1** Curing conditions for different curing conversions

<table>
<thead>
<tr>
<th>Curing conversion</th>
<th>Curing condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>65%</td>
<td>150 °C for 1.5 hours</td>
</tr>
<tr>
<td>75%</td>
<td>150 °C for 2 hours</td>
</tr>
<tr>
<td>80%</td>
<td>150 °C for 2.5 hours</td>
</tr>
<tr>
<td>85%</td>
<td>150 °C for 3 hours</td>
</tr>
<tr>
<td>90%</td>
<td>150 °C for 4 hours</td>
</tr>
<tr>
<td>95%</td>
<td>150 °C for 6 hours</td>
</tr>
<tr>
<td>99%</td>
<td>150 °C for 2 hours and 180 °C for 3 hours</td>
</tr>
<tr>
<td><strong>100%</strong></td>
<td>150 °C for 2 hours and 180 °C for 3 hours and 200 °C for 4 hours</td>
</tr>
</tbody>
</table>

*Fully post cured, the conversion near to 100%.*
The mechanical properties of epoxy resin with different curing conversions were tested to evaluate their relationship as shown in Fig. 2. Fig. 2a shows the impact strength of the samples with different curing conversions. With the increase in the curing conversion, the impact strength initially increased at the same time. Especially at 85%, the impact strength dramatically increased, which is nearly twice the value of 80%. After 90%, the impact strength changed little, even decreasing at 95% and 100%, i.e. the impact strength levelled off when the curing conversion was above 85%.

The influence of curing conversion on the average peeling strength of the epoxy resin using both unoxidized and oxidized (with black oxide layer) copper foil is shown in Fig. 2b. Maximum values appear at conversion between 80% and 95% both in the unoxidized copper clad and oxidized copper clad. It is generally accepted that the peel strength is highly dependent on the adhesive strength of the copper–resin interface and the flexibility of the matrix resin. In other words, the peel strength is closely related to the toughness of the materials.

With the increase in the curing conversion, more epoxy groups are polymerized or reacted with curing agents, which increases the crosslink density and lowers the chain mobility of the epoxy networks, and thus results in a higher modulus, higher tensile strength and lower elongation at break. Therefore, it can be easily inferred that there would be the highest value of peel strength at a specific curing conversion (not 100%) based on the factors mentioned above. This deduction is confirmed by our previous study, which demonstrated that the maximum peel strength is located at about 80–95% curing conversion.

3.2 Water sorption

In addition to thermal and mechanical properties, the curing conversion would also have a deep impact on the corrosion resistance and stability of epoxy materials. Moreover, water sorption is a critical property which is closely related to the performances mentioned above.

Gravimetric measurements. As epoxy materials are widely used in various industrial areas, two temperatures, 35 °C and 75 °C, were selected to study the water sorption behaviour as a simulation of normal RT and high temperature applications. Fig. 3 shows the gravimetric measurements of water sorption at 35 °C and 75 °C, and the equilibrium water contents \(M_e\) with different curing conversions obtained from this test are shown in Fig. 4a. At 35 °C, the equilibrium water content increased with conversion. However, a quite different tendency was observed at 75 °C: the equilibrium water content first decreased with the conversion, and then increased again after reaching the lowest value at 95%. Another curious result is the lower water sorption content of the 99% and 100% samples at high.
temperatures, which cannot be simply explained by previous knowledge. To discover the root cause of this type of unusual water sorption difference at high and low temperatures, we chose IR and DMA instruments to monitor the water sorption process, which will be discussed in the next part of this article.

In another aspect, the diffusion coefficient is an important index which affects the properties of epoxy materials. It is generally accepted that the behavior of water sorption curves in epoxy conforms to Fickian diffusion in the initial sorption process. The diffusion coefficients fulfill the following equation according to Fick’s second law: 

\[
\frac{M_t}{M_\infty} = \left(\frac{4}{L\sqrt{\pi}}\right)\sqrt{Dt}
\]  

where \(M_t\) is water sorption at time \(t\), \(M_\infty\) is the equilibrium value of the diffusing water at infinite time, \(D\) is the diffusion coefficient, and \(L\) is the thickness of the specimen.

Diffusion coefficients were calculated from the initial slope of these sorption curves by curve fitting according to eqn (4), the fitting curve of water diffusion of 65% at 35 °C is shown in Fig. 5 as an example. Fig. 4b displays the diffusion coefficient versus curing conversion at 35 °C and 75 °C. The diffusion coefficient decreased first with the curing conversion (reached the lowest values at 85–95% region), and then increased.

In previous works, it was found that the diffusion coefficient is mainly controlled by free volume, while polarity has a minor effect on diffusion coefficient. With the increase of curing conversion, the free volume decrease restricts the
Arrangement of the backbone and segments of epoxy networks because of the increase in $T_g$ and enlargement of the crosslink density, which results from the reaction of epoxy and amine groups. However, further curing leads to a fractional free volume increase. As a result, the diffusion coefficient first increased with the curing conversion, and then decreased when the epoxy was near fully cured. At a high temperature such as 75 °C, more free volume exists compared to that at lower temperatures. Thus, high temperatures favor the chain/disentanglement, and the diffusion coefficient has a higher value.

This contrary change of equilibrium water content may suggest a different water sorption mechanism at high and low temperatures. In order to well understand the diffusion mechanism of water sorption at high and low temperatures and the effect of water sorption on other properties, we selected specimens of conversion of 75%, 85%, 95%, and 100% as representations for other instrument tests.

**Diffusion behaviour at 35 °C.** The ATR-IR spectra of water diffusion in the DGEBA-DDS system at 35 °C are shown in Fig. 6, in which the IR spectra of absorbed water in the range of 3700–2800 cm$^{-1}$ reveals the increasing intensity of the OH vibration band (located at 3700–3000 cm$^{-1}$) as water diffuses into the epoxy networks.

2D correlation analyses were performed to study the water diffusion behaviour due to its significant advantages:

1. It has a higher distinguish ability than one-dimensional spectra, and thus one can distinguish some weak peaks, which are hard to be detected by one-dimensional spectra;
2. One is able to observe the specific sequence of certain events taking place in the system. The 2D correlation spectra in the range of 3700–3000 cm$^{-1}$ are shown in Fig. 7. In the synchronous spectra only one strong auto-peak was observed at 3400 cm$^{-1}$, which is assigned to the OH stretching band of water molecules. However, more information can be obtained from the corresponding asynchronous correlation spectra. Taking the asynchronous correlation spectrum of 100% as an example, two cross-peaks $\Psi(3400,3172) < 0, \Psi(3610,3172) < 0$ dominate the asynchronous map in the upper left triangle of this figure, which suggests there are three species of water molecules, located around 3610, 3400, and 3172 cm$^{-1}$, respectively.

In the research of water diffusion in polar polymer systems, four sorption peaks located at 3600 cm$^{-1}$, 3500 cm$^{-1}$, 3400 cm$^{-1}$ and 3200 cm$^{-1}$ were found through the infrared spectrum peak fitting method. Musto et al. assigned the four bands to water molecules without hydrogen bonds ($S_0$, 3600 cm$^{-1}$), with one hydrogen bond ($S_1$, 3500 cm$^{-1}$), and with double hydrogen bonds (loosely bonded $S_{2L}$, 3400 cm$^{-1}$; and tightly bonded $S_{2T}$, 3200 cm$^{-1}$), respectively. The difference of $S_{2L}$ and $S_{2T}$ is a result from the different strengths of the hydrogen bonds.

According to Noda’s rule, if $\Phi(p_1,p_2) > 0$, $\Psi(p_1,p_2) > 0$, band $p_1$ will vary prior to band $p_2$, and if $\Psi(p_1,p_2) < 0$, band $p_1$ will vary after band $p_2$. In the asynchronous correlation spectrum of 100%, $\Psi(3400, 3172) < 0$, $\Psi(3610, 3172) < 0$, which indicates that the change of $S_{2T}$ is always sooner than the change of $S_0$, $S_{2L}$. The results of the 2D correlation analysis for the ATR-IR are summarized in Table 2, in which the bond water molecules such as $S_{2T}$ or $S_{2L}$ changed prior to $S_0$.

Previous studies have demonstrated that water sorption in epoxy resins is controlled by two factors: polarity and free volume; the former one endows hydrogen bonding sites for

![Fig. 7 2D correlation spectra of water diffusion of DGEBA-DDS at 35 °C. (a) synchronous spectrum; (b) asynchronous spectrum.](image-url)
water molecules, while the latter one provides a path for water diffusion. In other words, the competition and coordination of these two factors decide the water sorption in epoxy resins. During the curing process, each primary amine group reacts with an epoxide group to form a linkage with one secondary amine group and one hydroxyl group; further reaction of the secondary amine with epoxide generates a tertiary amine and another hydroxyl group. In other words, with the increase in curing conversion, the polarity of the epoxy resin quickly increases at the same time. As for the water sorption at a low

Fig. 8  Near-IR spectra of water diffusion in DGEBA–DDS at 75 °C: (a) original spectra; (b) subtracted spectra.
investigate the behaviour of water diffusion at high temperatures, NIR experiments were performed at 75 °C. In Fig. 8, the IR spectra of absorbed water in the range of 7300–6300 cm⁻¹ and of 5400–4800 cm⁻¹ reveal the increasing intensity of the OH stretching vibration band (located at 7300–6300 cm⁻¹) and of the OH bending vibration band (located at 5400–48 000 cm⁻¹) as water diffuses into the epoxy networks. In the region of 7300–6000 cm⁻¹, the absorbance of three separate bands located around 7070, 6810, and 6560 cm⁻¹ increased with time in the subtracted spectra (Fig. 8b) of 75% and 85%. The results agreed well with Buijs’s and Musto’s studies, in which they assigned the stretching vibration peaks at 7080 cm⁻¹ to S₀, 6800 cm⁻¹ to S₁, and 6535 cm⁻¹ to S₂. However, only two bands located around 7070, 6810 cm⁻¹ were observed for 95% and 100%, which might indicate that there were no S₂ water molecules in the 95%, 100% samples.

2D correlation analysis was applied for the water diffusion at 75 °C as shown in Fig. 9. In Fig. 9a, there are three auto-peaks in 75% and 85%, which are located at 7080, 6810, and 6560 cm⁻¹, respectively. However, there are only two auto-peaks, which are located at 7080 and 6810 cm⁻¹ in 95% and 100%. The results indicate that three types of water molecules (S₀, S₁, and S₂) were observed in 75% and 85%, while there were only two types (S₀ and S₁) for 95% and 100%, which agree with the subtracted spectra. In the asynchronous spectrum of the OH stretching region, the peak of S₀ was split into two peaks: 7100, 7000 cm⁻¹.

One can find that the band located at a high frequency shifted to a higher frequency with water diffusing into the epoxy resin, suggesting that a blue-shift occurred in the OH stretching region shown in Fig. 8b. The 2D correlation analysis for NIR is summarised in Table 3. Clearly, S₀ changed prior to S₁ and S₂ at 75 °C, which is reverse to the sequence of water sorption at 35 °C.

When water sorption took place at a high temperature (75 °C), both chain/segment disentanglement and vibration of the side group are possible. In this case, as the epoxy group showed no change during the water sorption process, i.e., no chemical reaction takes place with the aid of water, thus we reason that water sorption is a result of chain rotation and the hydrogen bond forming process. The reorientation of the epoxy network first favours the diffusion of free water molecules through free volumes, and then chain ends further

![Image](image_url)

**Fig. 9** 2D correlation spectra of water diffusion of DGEBA–DDS at 75 °C: (a) synchronous spectrum of OH stretching region, (b) asynchronous spectrum of OH stretching region.

<table>
<thead>
<tr>
<th>Curing conversion</th>
<th>Synchronous spectrum</th>
<th>Cross-peak</th>
<th>Asynchronous spectrum</th>
<th>Diffusion order</th>
</tr>
</thead>
<tbody>
<tr>
<td>75%</td>
<td>Φ(7080,7080), Φ(6810,6810), Φ(6560,6560)</td>
<td>Φ(7080,6810) &gt; 0, Φ(7080,6560) &gt; 0, Φ(6810,6560) &gt; 0</td>
<td>Ψ(7000,6560) &gt; 0, Ψ(7000,6810) &gt; 0</td>
<td>S₀ &gt; S₁; S₀ &gt; S₂</td>
</tr>
<tr>
<td>85%</td>
<td>Φ(7080,7080), Φ(6815,6815), Φ(6560,6560)</td>
<td>Φ(7080,6815) &gt; 0, Φ(7080,6560) &gt; 0, Φ(6810,6560) &gt; 0</td>
<td>Ψ(7000,6560) &gt; 0, Ψ(7000,6815) &gt; 0</td>
<td>S₀ &gt; S₁; S₀ &gt; S₂</td>
</tr>
<tr>
<td>95%</td>
<td>Φ(7085,7085), Φ(6815,6815)</td>
<td>Φ(7085,6815) &gt; 0</td>
<td>Ψ(7000,6815) &gt; 0</td>
<td>S₀ &gt; S₁</td>
</tr>
<tr>
<td>100%</td>
<td>Φ(7085,7085), Φ(6800,6800)</td>
<td>Φ(7085,6800) &gt; 0</td>
<td>Ψ(7000,6800) &gt; 0</td>
<td>S₀ &gt; S₁</td>
</tr>
</tbody>
</table>
connect with diffused water molecules to form amine–water–amine (hydroxyl and epoxy) hydrogen bonds. From this point of view, one can expect that a large amount of chain ends with unreacted secondary/primary amine groups and epoxy groups would increase the possibility to form hydrogen bonds with water molecules. Thus, with the increase of curing conversion, the equilibrium water content decrease.

The tendency turn at ca. 95% may come from two reasons: (1) chain mobility drops greatly with curing conversion because of the sharp increase in $T_g$; (2) the amount of chain ends with unreacted groups quickly decreases when the epoxy is near fully-cured. Therefore, the equilibrium water content showed larger values in the low conversion region due to the physical-crosslinking consumed water; while getting larger again at 100% due to higher polarity and larger free volume.

3.3 Effect of water sorption on properties

Thermal–mechanical properties. To demonstrate the above hypothesis on the basis of the IR study, DMA was used to study the glass temperature of specimens before and after water saturation at 35 °C and 75 °C as shown in Fig. 10. The values of $T_g$ before and after water saturation are summarized in Table 4.

![DMA curves of DGEBA–DDS before and after water saturation](image)

**Table 4** The change of $T_g$ (°C) after water saturation at 35 °C and 75 °C

<table>
<thead>
<tr>
<th>Conversion</th>
<th>75%</th>
<th>85%</th>
<th>95%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>131</td>
<td>136</td>
<td>166</td>
<td>197</td>
</tr>
<tr>
<td>35 °C</td>
<td>119</td>
<td>120</td>
<td>137</td>
<td>167, 187</td>
</tr>
<tr>
<td>75 °C</td>
<td>115, 140</td>
<td>116, 143</td>
<td>134, 160</td>
<td>155, 191</td>
</tr>
</tbody>
</table>
Significant differences were observed in both cases as $T_g$ dramatically changed after water sorption. After water sorption at $35^\circ C$, the $T_g$ drops about $10-30^\circ C$ due to the plasticization effect of water molecules in the epoxy network, which mainly resulted from the destruction of intramolecular hydrogen bonding in the epoxy. With the increase of the water sorption content, the decrease of $T_g$ increased with curing conversion from $12^\circ C$ for 75% to $30^\circ C$ for 100%.

However, a quite different tendency of $T_g$ change was observed for the systems after water sorption at $75^\circ C$. Two $T_g$s were confirmed as tan $\delta$ split into two peaks for all the samples. The first $T_g$ resembled what was observed for the system after water sorption at $35^\circ C$, which can also be attributed to the plasticization effect caused by water molecules. However, the second $T_g$, which was located at a higher temperature showed interesting variations. Compared with the $T_g$ of the epoxy before water sorption, the second $T_g$ of the 75% and 85% sample increased, while the $T_g$s of the 95% and 100% sample decreased ca. $6^\circ C$. This type of $T_g$ increase for sample 75% and 85% clearly results from the physical crosslinking of water molecules with the chain ends (or functional groups) through hydrogen bonds, which causes a little change in the curing conversion because epoxy groups show minor changes during the water sorption process. The strength of hydrogen bonding would decrease with

![Bode plots of EIS spectra, samples were immersed for 1 h prior to measurement: (a) 35 °C, (b) 75 °C.](image-url)
the increase in temperature, and dramatically decrease when the temperature is beyond the $T_g$. In our study, the $T_g$ of epoxy resins is considerably larger than 75 °C, therefore, the effect of the hydrogen bonding strength with temperature could be minimized. For high curing conversion such as 95% and 100%, the hydrogen bond is looser than the chemical bond between the amine and the epoxy. Therefore, the $T_g$ drops a little, which is relatively different from the plasticization effect of water as the latter causes a more substantial $T_g$ decline.

The results from the DMA study before and after water sorption at high and low temperatures could verify the speculation from the IR study. At a high temperature such as 75 °C, the chain reorientation favours the sorption of water and the formation of hydrogen bonds. Chain disentanglement reduces the free energy of the water–epoxy system, which results in higher equilibrium water contents compared to that at 35 °C. Thus, the value of first $T_g$ is a little lower than that of the system after water sorption at 35 °C.

**Corrosion resistance.** As the water sorption shows great dependence on the curing conversion at both high and low temperatures, one would expect some differences on the corrosion resistance of epoxy materials as coatings and adhesives.

EIS is widely employed to predict the corrosion resistance of coatings. The EIS experiments were performed at 35 °C and 75 °C. Considering the measuring range of our electrochemical workstation, we maintained the thickness of the coatings around 100 µm, as a result, the corrosion rate is faster than systems with thick coatings. The Bode plots of EIS spectra with immersion time at 35 °C and 75 °C are presented in Fig. 11. The reduced impedance modulus with immersion time should be attributed to the sorption of NaCl solution by the coatings. At 35 °C, except for 85%, the impedance modulus of 75%, 93% and 100% significantly changed after 20 hours. At high temperature of 75 °C, as the thickness of coatings is quite thin, the rate of water diffusion to the metal/coating interface is so fast that peeling of the coatings occurred after only 9 hours, after that the impedance modulus did not significantly change.

The impedance modulus at low frequency (0.1 Hz or 1 Hz) serves to estimate the corrosion protection of a coated metal. In this article, we used the value $\log|Z|$ at 0.1 Hz as a function of exposure time to evaluate the corrosion resistance performance of the coatings as shown in Fig. 12. The impedance modulus decreased faster at 75 °C than that at 35 °C, as the diffusion coefficient of 75 °C was considerably larger than that of 35 °C. For both temperatures, the coating corrosion resistance shows a fluctuation with curing conversion. Better corrosion resistance appeared in the conversion region of 75–85% for the samples at 35 °C, and 85–95% at 75 °C. According to the literature, coatings with a lower equilibrium water content show better corrosion resistance. Considering the equilibrium water content from the water sorption study, in which the equilibrium water content showed a minimum value corresponding to the corrosion test at both temperatures, i.e. at the curing conversion of 75–85% and 85–95%, the primary cause of coating corrosion is water diffusion at the metal-coating interface, thus a stronger strength metal-coating interface would lead to a higher corrosion resistance for coatings. The maximum values of peeling strength appear at conversion between 80% and 95%. Combining the two factors, the conversion of ca. 85% shows the best corrosion resistance.

**4. Conclusion**

Curing conversion of epoxy resins showed a close relationship with the thermo-mechanical, water sorption, and corrosion resistance properties of the materials.

Both the storage modulus and $T_g$ increased with curing conversion, and the growth of $T_g$ with curing conversion could be well described by the DiBenedetto equation.

Water diffusion coefficient by gravimetric measurements decreased with curing conversion in the low conversion range, and then increased as the free volume of the epoxy changed, which first decreases with curing conversion and increases when near fully cured.

The equilibrium water content increased with curing conversion at 35 °C, but showed a different tendency at 75 °C. The 2D-dimension IR analysis showed $S_2$ diffused prior to other types water molecules at 35 °C, while free water ($S_0$) diffused prior to bonded water ($S_1$ and $S_3$) at 75 °C. The $T_g$ was reduced after water saturation at low temperatures, while physical crosslinking took place among the water molecules and the epoxy resin at 75 °C, which resulted in the increase of the second $T_g$ in low curing conversion region.
Polarity and free volume influences the equilibrium water content. The equilibrium water content at 35 °C increased due to the increase in polarity, while the chain disentanglement and hydrogen bonds resulted in a higher water content in the low curing conversion region when water sorption occurred at 75 °C.

Both the mechanical properties and corrosion resistance studied by EIS experiments showed an optimized performance regime at a curing conversion close to ca. 85% due to the balanced property of water sorption and crosslink density.

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**References**

49 Q. Chen, G. Yang, Y. Wang, X. Wu, H. Kurosu and I. Ando, 
50 B. M. Fernandez-Perez, J. A. Gonzalez-Guzman, S. Gonzalez 
2079.
51 J. J. Santana, J. E. Gonzalez, J. Morales, S. Gonzalez and 
52 F. L. Floyd, S. Avudaiappan, J. Gibson, B. Mehta, P. Smith, 
53 J. J. Suay, M. T. Rodriguez, K. A. Razzaq, J. J. Carpio and 
54 J. M. McIntyre and H. Q. Pham, Prog. Org. Coat., 1996, 
27(1–4), 201–207.
55 A. Amirudin and D. Thierry, Prog. Org. Coat., 1995, 26(1), 
1–28.
57 G. Bierwagen, D. Tallman, J. P. Li, L. Y. He and C. Jeffcoate, 
58 E. Potvin, L. Brossard and G. Larochelle, Prog. Org. Coat., 