Contributions of the Side Groups to the Characteristics of Water Absorption in Cured Epoxy Resins

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Introduction

Owing to their eminent mechanical and electrical properties, epoxy resins are widely used as structural materials in the aerospace industry and for packaging- and coating applications in the microelectronics industry. Because they are often used in a humid environment, and the moisture absorbed in the cured epoxy resins generally degrades the properties of the materials, the behavior of moisture adsorption and transport in epoxy and epoxy-based composites has received much attention over the last two decades.1–5

O-Cresol novolac epoxy resin cured with phenol novolac resin (NOV) is an important encapsulating material for integrated circuit chips.6 The water sorption of the cured resin (EP) is ca. 2 wt.-%7,8 The absorbed water can not only deteriorate the thermal and mechanical properties, the structural stability of the encapsulating material, but also initiate corrosion in the aluminum patterns of the chips.9 Therefore, resins with low water sorption are strongly demanded by the electronic encapsulating industry.

Although it has been illustrated that free volume9–11 and polarity12 are the two intrinsic factors that determine the absorption and transport of moisture, it is difficult to separate the effect of polarity from that of free volume.13 On the other hand, though the effect of side groups on water absorption has scarcely been reported, it may play an important role in this process.

In the present work, to study the effects of side group on water absorption, a series of epoxy resins was cured separately with esterified phenol novolac resin and phenol novolac resin. Thus, the hydroxyl group of phenol novolac resin was replaced by a CH3COO− group, a CH3CH2CH2COO− and a C6H5CH2COO− group. The cured resins were named EP, EPA, EPB and EPP.
tively. Fourier transform infrared (FT-IR) spectroscopy showed that there were no hydroxyl groups and only ester functional groups in the cured resins cured with the esterified phenol novolac resins. The influence of the side groups on the water absorption behavior of the cured epoxy resins was investigated using a gravimetric method, DSC, PA and BET adsorption.

**Experimental Part**

**Materials**

O-cresol (2-methyl phenol) novolac epoxy resin (YDCN-702p from Tohto Kasei, Japan, epoxy equivalent: 200 ~ 230 g · eq⁻¹) and Novolac (H-1, from Sumitomo, Japan, hydroxyl equivalent: 107 g · eq⁻¹) were used in this work. The esterified curing agents were synthesized separately from NOV and acetic anhydride, butyric anhydride and phenylacetyl chloride. 2-Methylimidazole (2MI, from Wuhan Pharmaceutical Co., China) was used as curing accelerator.

**Sample Preparation**

The epoxy resins were cured by the curing agents according to the stoichiometric ratios with 0.5% of 2MI. The fresh mixture of the raw materials was dissolved in acetone (AR grade). Then the solution was poured into a 50 mm × 20 mm × 20 mm aluminum mold. After being left in the air at room temperature for 1 d, the resin was cured in a vacuum oven at 45 °C/15 min, 80 °C/15 min, 120 °C/3 h, 150 °C/2 h, 180 °C/2 h, and finally cooled slowly down to room temperature. DSC showed that there was no residual heat after curing. The chemical structures of the cured resins are shown in Scheme 1.

**Sorption Method**

Prior to the absorption experiments, the sample sheets (10 mm × 10 mm × 1 mm) were polished, rinsed with distilled water, and then dried under vacuum oven at 85 °C for a week. Water sorption of the resin as a function of immersion time was monitored by the gravimetric method. The samples were periodically removed from the water, wiped down and quickly weighed on a TG332A microbalance (accuracy: ±0.01 mg). The water sorption (uptake at time \( t \), \( M_t \)) of the sample is defined as

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

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

**BET Adsorption and PA Experiment**

The BET surface area of the sample was measured with a Micromeritics ASAP 2000 system under liquid N\(_2\) using N\(_2\) as the adsorbate. The PA experiment\(^{[14]}\) was conducted on a multichannel analyzer data buffer (Ortec Adcam model) at room temperature. The probe consists of BaF\(_2\) crystal and XP2020Q PMT. 20 μCi Na\(^{22}\)Cl was directly deposited on one of the samples and then sandwiched between two identical pieces of the samples. The positron annihilation lifetime spectra were analyzed by PATFIT.

**Results and Discussion**

**Characteristics of Water Absorption**

The plots of \( M_t/M_\infty \) versus \( t^{1/2}/d \), where \( d \) is the sample thickness, at 20 °C are shown in Figure 1.

The results are listed in Table 1. Table 1 shows that at all experimental temperatures, the \( M_\infty \) of the four samples takes the following order, EP \( A \) \( \geq \) EPA \( \geq \) EPP \( A \) \( \geq \) EB.

The diffusion coefficient \( D \) can be calculated according to the slope of the curve in Figure 1:

\[
D = \frac{S}{S^2 \pi/16}
\]

where \( S \) is the slope at the initial stage of the absorption.\(^{[15]}\) At 20 °C and 40 °C the order of \( D \) can be presented as, EPB > EPA > EPP > EP, while at 60 °C and 80 °C, it changes to, EPB > EP > EPP > EP.
induced by hydroxyl groups. However, the weak interaction of the side groups and the internal plasticizer of the network and methyl butyrate and methyl benzorate at 20°C, therefore, the sequence measured by DSC has the following order, T_g of the cured resins is much lower than that of EP, because of the high polarity of the hydroxyl group. Though the polarities of the three esterified systems are very similar, the flexibility of these cured resins is different as can be found by comparing their T_g. The aliphatic group of the side group is hydrophobic and pliant, and the accessible volume of absorption is sheltered and reduced by the movement of the side groups. The “shielding effect” of the bulky side groups to water is greatly influenced by the flexibility of the side groups, and is most significant in EPB, the resin with the lowest T_g. Therefore, for the three esterified systems, at 60 and 80°C, the decrease in the values of M_w shows the same tendency as that of the T_g’s, while at 20 and 40°C, the M_w of EP is slightly greater than that of EPP. This may be due to the reason that the flexibility of the C6H5CH2COO– group is greatly influenced by the temperature. This difference is also shown in the variation of the D for EPP and EPA.

The T_g of EP is the highest, inferring a compact structure caused by the strong intramolecular interaction induced by hydroxyl groups. However, the T_g of the esterified systems is much lower than that of EP, because of the weak interaction of the side groups and the internal plasticization of the ester functional groups. Furthermore, because the polarities of the ester functional groups and chemical structures of the networks are both similar among the esterified systems, it would seem that the order of the T_g is related to that of the flexibility of the side groups at T_g temperatures. Hence, the flexibility of the three ester functional groups is expected to be in the following order: EPB > EPP > EPA.

Table 1. Results of water uptake at various temperatures for the four epoxy resins.

<table>
<thead>
<tr>
<th>T/°C</th>
<th>M_w%</th>
<th>D x 10^(-9) cm^2·s^(-1)</th>
<th>M_v%</th>
<th>D x 10^(-9) cm^2·s^(-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.13</td>
<td>2.4</td>
<td>0.77</td>
<td>9.5</td>
</tr>
<tr>
<td>40</td>
<td>2.17</td>
<td>6.9</td>
<td>1.00</td>
<td>23.2</td>
</tr>
<tr>
<td>60</td>
<td>2.18</td>
<td>24.5</td>
<td>1.19</td>
<td>47.0</td>
</tr>
<tr>
<td>80</td>
<td>2.22</td>
<td>55.0</td>
<td>1.73</td>
<td>89.5</td>
</tr>
</tbody>
</table>

Table 2. T_g of the cured resins.

<table>
<thead>
<tr>
<th>EP</th>
<th>EPA</th>
<th>EPB</th>
<th>EPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>458</td>
<td>420</td>
<td>381</td>
<td>395</td>
</tr>
</tbody>
</table>

The M_w of the cured resins follows the same ordering as that of the T_g. Therefore, it may be concluded that the M_w increases with the increasing of the polarity of the side groups, and the increase of the flexibility of the side groups is unfavorable for water uptake. The M_w of EP is much higher than that of the esterified systems owing to the high polarity of the hydroxyl group. Though the polarities of the three esterified systems are very similar, the flexibility of these cured resins is different as can be found by comparing their T_g. The aliphatic group of the side group is hydrophobic and pliant, and the accessible volume of absorption is sheltered and reduced by the movement of the side groups. The “shielding effect” of the bulky side groups to water is greatly influenced by the flexibility of the side groups, and is most significant in EPB, the resin with the lowest T_g. Therefore, for the three esterified systems, at 60 and 80°C, the decrease in the values of M_w shows the same tendency as that of the T_g’s, while at 20 and 40°C, the M_w of EP is slightly greater than that of EPP. This may be due to the reason that the flexibility of the C6H5CH2COO– group is greatly affected by the temperature. This difference is also shown in the variation of the D for EPP and EPA.

In the case of EP, M_w 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. This difference may be explained by two reasons:

First, the thermal effect is different between EP and the three esterified resins. The process of water absorption can be simply depicted as the following two steps according to their different thermal effects: bulk dispersion and specific interaction (Scheme 2).

In the scheme, R represents the resin.

The process of dispersion of bulk water into epoxy resins is endothermic (Q_1) and there are no evident differences among the values of Q_1 of the four samples. While, the specific interaction between water and the polar sites of the resin is exothermic (Q_2) (typical hydrogen bond energy is 12–33 kJ · mol^(-1)). The total thermal effect (Q) is the combination of Q_1 and Q_2.
In the case of EP, the hydroxyl groups and water molecules could form strong hydrogen bonds. Q in EP resin is not evident because of the balance between $Q_1$ and $Q_2$, while in the three esterified samples, the strength of hydrogen bond of the ester functional groups with water molecules is weaker than that in EP. As a result, $Q_2$ of the three systems are much smaller than that of EP. Therefore, an increase in temperature is beneficial to water absorption of the three esterified systems, but apparently has little effect on that of EP.

Secondly, the mobility of the ester functional groups is enhanced with increase in temperature. Thus, the shielding effect and obstruction to water molecules may be reduced at higher temperatures. Some volumes of nanopores which are sheltered and inaccessible to water molecules at low temperatures are revealed by movement of ester functional groups and become open to water molecules. Hence, the total accessible volume increases with temperature. However, in the case of EP resin, the total accessible volume is almost unchanged because of the difficulty of the movement of the hydroxyl groups, which is restricted by the hydrogen bonds.

Although the affinity of water molecule for the resin can increase the water uptake, it may also retard the transport of water. As shown in Table 1, the $D$ of EP is lower than that of the other three resins.

The density of EPB at the experimental temperatures is the highest of the three. At 20°C and 40°C, the value of $D$ of EPA is slightly higher than that of EPP, however, at 60°C and 80°C, the values of $D$ of EPP are higher than those of EPA. This is also owing to the variation of flexibility of the side groups as mentioned above. Therefore, during a sorption process, a glassy polymer has to adjust its polymer segments to adapt to the transport of the water, which is related to the flexibility of the side groups. These results may suggest that besides polarity, $D$ is greatly influenced by the flexibility of the side group: the greater the flexibility of the side group, the higher the $D$ of water diffusion in the resin.

It is obvious that the mechanism and kinetics of water transport in EP are different from the three esterified systems. In the case of EP, the absorption and transport are mainly governed by the specific interaction between epoxy resin and water molecules. But in the case of esterified epoxies, since the polarity of ester functional group is much less than that of a hydroxyl group, the shielding effect and flexibility of the side ester functional groups will play a leading role in water transport. In brief, the higher the polarity of the side group, the lower the value of $D$; the higher the flexibility of the side group, the higher the value of $D$.

**BET Surface Area**

BET adsorption of nitrogen was conducted in order to evaluate the accessible surface area of the samples.

From the BET results listed in Table 3, it was found that EPB has the largest surface area (0.9341 m² g⁻¹), which means that the volume fraction of nanopores in EPB resin is the largest. However, the $M_\infty$ of EPB is much less than those of the other epoxy resins. There is no evident dependence of water absorption and diffusion on the volume of nanopores.

**Size and Number of Nanopores**

In the PA experiment, when positrons were transmitted into polymers, they formed a positronium which had two spin states ($\sigma$-Ps and $p$-Ps). The longest lifetime component ($\tau_2, I_2$) is due to the annihilation of $p$-Ps with electrons. $\tau_2$ is related to the pore size of the nanopores of the polymer, and $I_2$ is often treated as a measure of the number of the pores.\(^{[21, 22]}\) The results are shown in Table 4. At 20°C and 40°C, the values of $D$ are in the following order: EPB > EPA > EPP > EP. The average size of nanopores detected by PA shows the same order. Soles and Yee recently found that there is a mild exponential dependence of $D$ on the average nanopores size at low temperatures.\(^{[23]}\) Suriki et al.\(^{[22]}\) also reported that a correlation exist between the absorption rate and the size of the average holes. But there is not enough evidence to prove that $D$ is mainly dependent on the size and number of nanopores.

<table>
<thead>
<tr>
<th>Table 3. PA results at room temperature.</th>
<th>Sample</th>
<th>EP</th>
<th>EPA</th>
<th>EPB</th>
<th>EPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$/ns</td>
<td>1.6475</td>
<td>1.7667</td>
<td>1.8887</td>
<td>1.7424</td>
<td></td>
</tr>
<tr>
<td>$I_2$/%</td>
<td>20.9</td>
<td>18.7</td>
<td>21.75</td>
<td>17.2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4. BET adsorption of nitrogen.</th>
<th>Sample</th>
<th>Area m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP</td>
<td>0.8931</td>
<td></td>
</tr>
<tr>
<td>EPA</td>
<td>0.7851</td>
<td></td>
</tr>
<tr>
<td>EPB</td>
<td>0.9341</td>
<td></td>
</tr>
<tr>
<td>EPP</td>
<td>0.5704</td>
<td></td>
</tr>
</tbody>
</table>
Conclusion

By designing a series of epoxy resins, we were able to investigate the effects of polarity and microstructure of the networks on the water uptake and diffusion in epoxy resins. The difference among the resins in uptake and diffusion of water can be explained as follows:

1. The equilibrium water uptake ($M_v$) is mainly determined by the characteristics of the side groups. The higher the polarity, the higher $M_v$; the better the flexibility, the lower $M_v$. There is no evidence showing a dependence of $M_v$ on the volume of nanopores.

2. $M_v$ of EP varies slightly with temperature raging from 20 $^\circ$C to 80 $^\circ$C. On the contrary, $M_v$ of the esterified systems increases significantly with temperature.

3. With the EP resin, the kinetics of transport is mainly controlled by the specific interaction between water and epoxy. But in the esterified systems, diffusion and transport of water molecules are greatly influenced by the extent of difficulty of adjustment of the segmental conformation, which is greatly dependent on the flexibility of the side ester groups. Therefore, on increasing the flexibility of ester functional group, $D$ decreases.

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