



Two-Stage Moisture Absorption Behavior and Hydrolysis of Cured Dicyanate Ester Resins

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Abstract

A two-stage moisture absorption behavior for the cured 4,4-dicyanato 1,1-diphenolethane (DCDPE) resins was found when they were exposed to 60°C/100%RH environment. The first stage followed the Fickian diffusion, whereas the secondary stage was a swelling-controlled diffusion in that the diffusion coefficient was decreased with time. With increasing the sample thickness, the two-stage absorption behavior became less discernible. After long term exposure to moisture, DCDPE resins were prone to hydrolysis to form voids in the networks. When chromium acetylacetonate (Cr(acac)₃) was incorporated in the resin formulations as a curing accelerator, it also accelerated the hydrolysis, facilitating the formation of voids.

Introduction

Cyanate ester resins are a thermosetting material with a low dielectric constant, high glass transition temperature, and good mechanical and processing properties. They are often used as a resin matrix for multi-layer electric circuit boards in the microelectronics industry [1]. However, one of the major disadvantages for cyanate ester resins is their rather poor hydrolytic decomposition resistance [1–4], causing the blistering of networks in solder temperature if they have not been dried in advance. This decomposition has been suggested to result from the larger free volume in the cured network structure, allowing the water molecules to pass through [2].

The moisture absorption behavior of thermosetting resins and their composites has been studied extensively since the 1970s [5–9]. For a rectangular specimen, the Fickian second law, that the diffusion coefficients are assumed to be independent of the moisture concentration, has often been employed to describe the moisture absorption behavior. Accordingly, the following partial differential equation for moisture diffusion was solved analytically with proper boundary conditions,

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2}, \quad (1)$$

where $C(t, x, y, z)$ is the moisture concentration in the Cartesian coordinates (x, y, z) of the specimen at time t ; D_x , D_y , and D_z are the diffusion coefficients at the x , y , and z directions. For isotropic materials, $D_x = D_y = D_z$. Thus, the amount of moisture absorption M_t of the specimen at

time t can be solved from Equation (1) [7, 8]

$$\frac{M_t - M_0}{M_m - M_0} = 1 - \frac{8}{\pi^2} \left[1 - 4\sqrt{\frac{D_x t}{\pi l^2}} \right] \left[1 - 4\sqrt{\frac{D_x t}{\pi n^2}} \right] \times \left\{ \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp \left[-(2i+1)^2 \pi^2 \frac{D_x t}{h^2} \right] \right\}, \quad (2)$$

where M_0 and M_m are the initial and maximum moisture absorptions respectively; l , n , and h are the length, width, and thickness of the specimen. By plotting M_t versus \sqrt{t} , the initial linear portion can be used to calculate the apparent diffusion coefficient D by [7]

$$D = \pi \left(\frac{h}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2, \quad (3)$$

where M_1 and M_2 are the amount of moisture absorption at time t_1 and t_2 respectively, taken from the linear portion of the plot. Therefore, D_x in Equation (2) can be estimated by

$$D_x = D \left(1 + \frac{h}{l} + \frac{h}{n} \right)^{-2}. \quad (4)$$

If the experimental data are fit by Equation (2) with estimated D_x , the moisture absorption behavior of the specimen is referred to as Fickian diffusion.

Although the anomalous behavior of moisture absorption of cured cyanate ester has been frequently reported [2, 10–12], how it deviates from the Fickian diffusion has not been fully investigated. In this contribution, we found that the initial moisture absorption of cured 4,4-dicyanato 1,1-diphenolethane (DCDPE) resins followed the Fickian diffusion but deviated after the specimens began to swell. Thus, a

two-stage moisture diffusion model was provided to describe the moisture absorption behavior of cyanate ester resins. After long term exposure to moisture, the voids formed due to the hydrolysis of resin networks was observed by scanning electron microscopy (SEM). Their degree of hydrolysis was then estimated by Fourier-transform infrared (FTIR) spectroscopy and in terms of sample thickness and the incorporation of metal complex accelerators.

Experimental

Materials

4,4-dicyanato 1,1-diphenolethane (DCDPE, Ciba Geigy L10) was used as received. DCDPE incorporating 0.5 phr chromium acetylacetonate ($\text{Cr}(\text{acac})_3$, Hayashi Japan) was prepared by mixing the ingredients at room temperature until $\text{Cr}(\text{acac})_3$ was completely dissolved. The DCDPE resins with and without incorporating $\text{Cr}(\text{acac})_3$ were heated to 80°C and degassed under vacuum before cast into rectangular molds made from silicone rubber. The specimens were cured according to the following schedule: ~ 2 h/ 100°C (until gelled) + 4 h/ 160°C + 4 h/ 220°C . Cured specimens with various thicknesses after cutting and sanding to 28.0×14.0 mm dimensions were placed in a desiccator at 60°C for drying. Until the specimens were dried to a constant weight (~ 2 weeks), they were placed in an environment chamber controlled at $60^\circ\text{C}/100\%RH$. At chosen time intervals the specimens were removed from the chamber and had their weight and dimensions measured immediately. All the moisture absorption experiments were completed after 2800 h. The re-dried samples for FTIR tests and scanning electron microscopy (SEM) investigations were placed in a desiccator at 60°C until dried to a constant weight.

Characterization

The density of the specimens was measured by using the pycnometric method with distilled water as a known density liquid; the accuracy was up to 0.001 g cm^{-3} . The sample dimensions were measured by micrometer at marked places with accuracy up to 0.01 mm. Then, the volumetric variations during the moisture absorption were estimated from the changes of length, width and thickness of the specimens. FTIR spectra were recorded on a Jasco-300E Fourier-transform IR spectrometer with a KBr disc. Izod impact specimens were prepared and fractured by a CSI model pendulum impact tester. Their fractured surfaces for SEM were gold-sputtered and investigated in a JSM-T1000 scanning electron microscope.

Results and Discussion

Two-Stage Moisture Absorption

Figure 1(a) shows the moisture gain of a 0.45 mm-thick DCDPE cyanate ester resin exposed to a $60^\circ\text{C}/100\%RH$

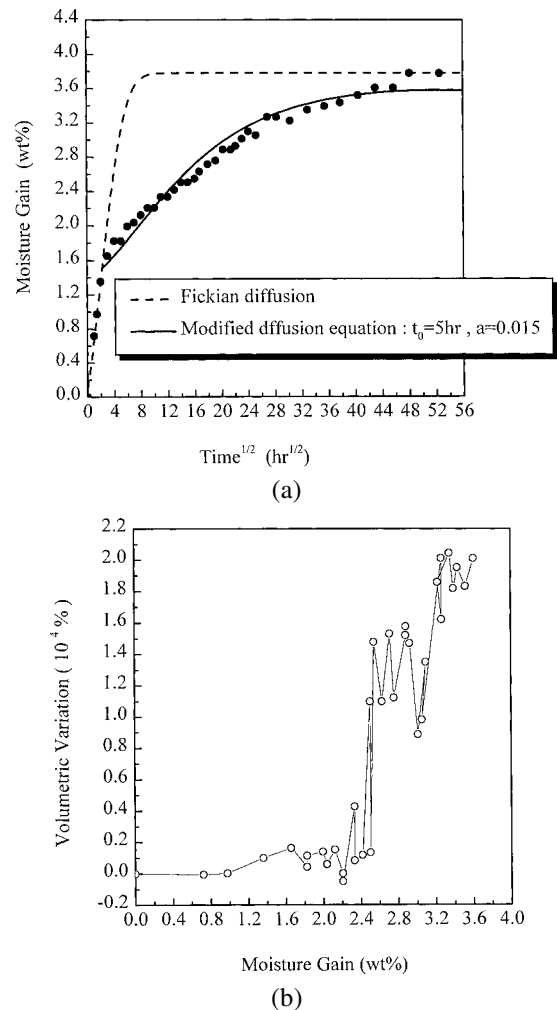


Figure 1. (a) Moisture gain of 0.45 mm-thick DCDPE cyanate ester resins exposed to $60^\circ\text{C}/100\%RH$ as a function of square root of time, and (b) the concurrent volume change vs. moisture gain of the specimens.

environment as a function of square root of time. By using Equation (2) to fit the experimental data, we found the initial 5 h moisture absorption was fitted quite well with $D_x = 1.20 \times 10^{-3} \text{ mm}^2/\text{h}$ ($D = 1.32 \times 10^{-3} \text{ mm}^2/\text{h}$). After that, the data significantly deviated from the Fickian along with a substantial increase in volume of the specimen, as seen in Figure 1(b). Apparently, the deviation from the Fickian was due to swelling. Once the specimen was saturated with water, swelling stopped unless hydrolysis occurred. Similar phenomena have long been reported for other polymer materials and referred to as the so-called “dual sorption model”, meaning that the absorbed water is divided into mobile water (or free water) and bound water [13–18]. The behavior of mobile water was described by Henry’s law, whereas that of bound water was described by the Langmuir theory of absorption [19]. Therefore, we assumed that in the secondary stage of diffusion, the diffusion coefficient D_x decreases with time by

$$D'_x = D_x \left[1 - \left(\frac{t - t_0}{\tau} \right)^a \right], \quad t - t_0 \leq \tau, \quad (5)$$

where t_0 is the time that diffusion began to deviate from the Fickian; τ is the time span from t_0 to t_f , the final time by

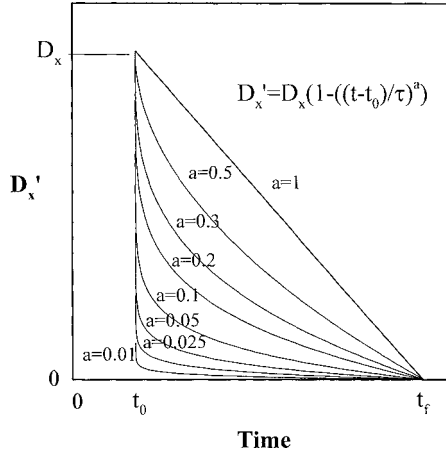


Figure 2. Diffusion coefficient D'_x in Equation (5) as functions of time and 'a'.

which the specimen is saturated (2800 h was chosen in this study); a is the parameter that indicates the degree of deviation from the Fickian. The deviation of D'_x from D_x with time as a function of 'a' was plotted in Figure 2. In general, the extent of deviation is increased with decreasing 'a'. By using D'_x to substitute for D_x in Equation (1), we can still have an analytical solution for $C(x, y, z, t)$. Then, the amount of moisture absorption of the specimens at time t , can be estimated by

$$M_t = A \int_0^l \int_0^n \int_0^h C(x, y, z, t) dx dy dz, \quad (6)$$

where A is the conversion factor. Thus, by assuming $t \geq t_0$,

$$\begin{aligned} & \frac{M_t - M_0}{M_m - M_0} \\ &= 1 - \frac{8}{\pi^2} \left[1 - 4 \sqrt{\frac{D_x \left(t - \frac{\tau}{a+1} \left(\frac{t-t_0}{\tau} \right)^{a+1} \right)}{\pi l^2}} \right] \times \\ & \times \left[1 - 4 \sqrt{\frac{D_x \left(t - \frac{\tau}{a+1} \left(\frac{t-t_0}{\tau} \right)^{a+1} \right)}{\pi n^2}} \right] \times \\ & \times \left\{ \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp \left[-(2i+1)^2 \pi^2 \times \right. \right. \\ & \left. \left. \times \frac{D_x \left(t - \frac{\tau}{a+1} \left(\frac{t-t_0}{\tau} \right)^{a+1} \right)}{h^2} \right] \right\}. \quad (7) \end{aligned}$$

Equation (7) was used to fit the experimental data in Figure 1(a). The result of fitting by assuming $t_0 = 5$ hr and $a = 0.015$ was good up to 2000 h. After then, the experi-

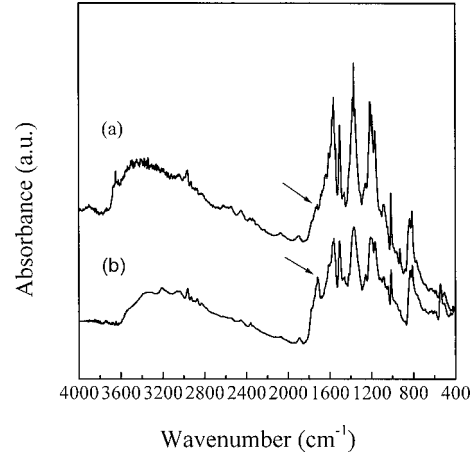
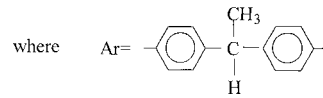
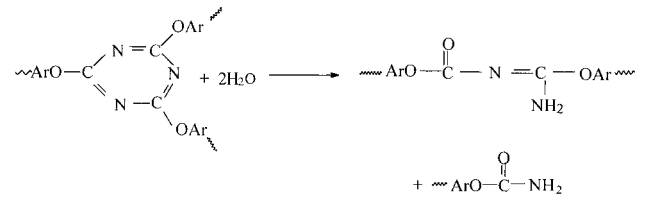


Figure 3. FTIR spectra of DCDPE cyanate ester resin: (a) without moisture absorption, and (b) after being exposed to 60°C/100%RH for 2800 h and re-dried.

mental data began to deviate and the specimen was further swollen (see Figure 1).

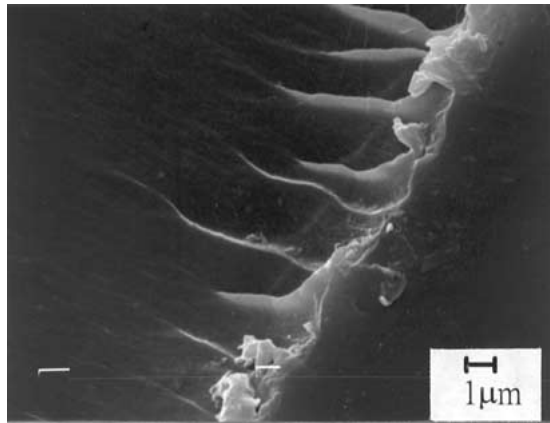
The FTIR spectra of the re-dried specimens after absorbing moisture for 2800 h are shown in Figure 3. The appearance of the IR peak at 1714 cm^{-1} contributed by the carbonyl groups in dimers [20] indicates that the reverse reaction of trimerization of the isocyanate groups shown below might have occurred due to the hydrolysis of the triazine rings in the networks;



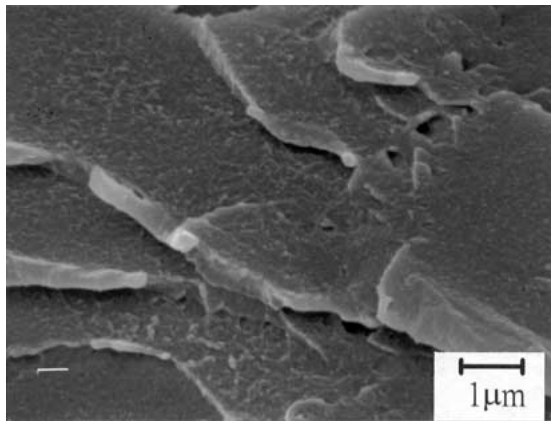
The dimers of DCDPE resins formed in the early cure stage have been identified by FTIR, ^1H - and ^{13}C -NMR spectroscopy in our previous study [20]. They were rather stable after formation and could remain intact with the DCDPE monomers at room temperature for at least a week.

The re-dried specimens were then subjected to the Izod impact test with the fracture surface investigated by SEM. Figure 4 shows that the re-dried samples have a rougher and ductile fracture surface compared to those without moisture absorption. Apparently, hydrolysis by long term exposure to moisture might have produced microvoids in the networks.

Figure 5(a) shows the moisture gain of a 2.5 mm-thick DCDPE cyanate ester resin exposed to a 60°C/100%RH environment as a function of square root of time. Compared to Figure 1(a), the moisture absorption of the thick sample in the secondary stage of diffusion deviated less from the Fickian. The initial moisture absorption was fit with $D_x = 3.03 \times 10^{-3} \text{ mm}^2/\text{h}$ ($D = 4.57 \times 10^{-3} \text{ mm}^2/\text{h}$) until 90 h (t_0). By using Equation (7) with $a = 0.2$ to fit the secondary stage of moisture absorption, the result was also



(a)



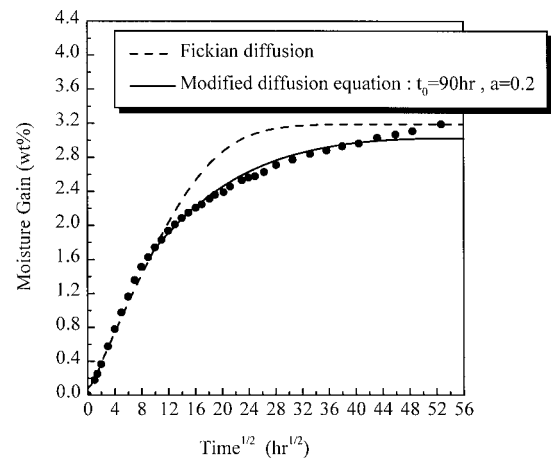
(b)

Figure 4. SEM micrographs of fracture surface of DCDPE cyanate ester resin: (a) without moisture absorption, and (b) after being exposed to 60 °C/100%RH environment for 2800 h and re-dried.

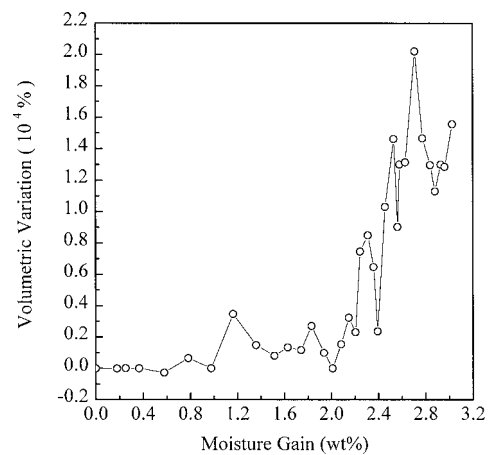
good up to 2000 h. The percentage of absorbed moisture at t_0 and the abrupt increase of volume of the specimens after t_0 (see Figure 5(b)) were similar to those of the thin specimens. The increase of D_x with the thickness is also shown in Figure 6. Moreover, 'a' and ' t_0 ' increased with the thickness shown in Figure 7 indicating that the deviation from the Fickian in the secondary stage of diffusion was less. On the other hand, although the diffusion coefficient increased with the sample thickness, the moisture gain of the specimens after exposure to a 60 °C/100%RH environment for 2800 h decreased (see Figure 8). By choosing the IR peak at 1014 cm^{-1} contributed by the aromatic C-H groups as a reference peak (see Figure 3), we also found that the degree of hydrolysis (indicated by $I_{1714\text{cm}^{-1}}/I_{1014\text{cm}^{-1}}$) of the re-dried specimens decreased slightly with the thickness (see Figure 9). Because the hydrolysis of the network created voids, the moisture diffusion did not completely stop after the specimens were saturated with moisture. This explains why the moisture gains in Figures 1(a) and 5(a) began to deviate from the prediction by Equation (7) after 2000 h.

Effect of Incorporating $\text{Cr}(\text{acac})_3$

$\text{Cr}(\text{acac})_3$ is a moderate accelerator for curing DCDPE cyanate ester resins [20]. Moreover, in epoxy technology



(a)



(b)

Figure 5. (a) Moisture gain of 2.5 mm-thick DCDPE cyanate ester resins exposed to 60 °C/100%RH as a function of square root of time, and (b) the concurrent volume change vs. moisture gain of the specimens.

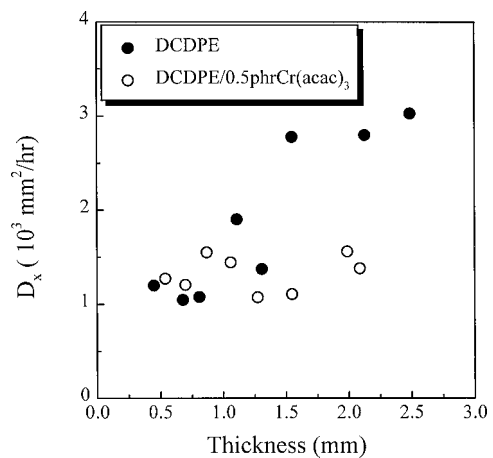


Figure 6. Diffusion coefficient D_x at 60 °C/100%RH as a function of sample thickness for (●) DCDPE cyanate ester resins and (○) DCDPE incorporating 0.5 phr $\text{Cr}(\text{acac})_3$.

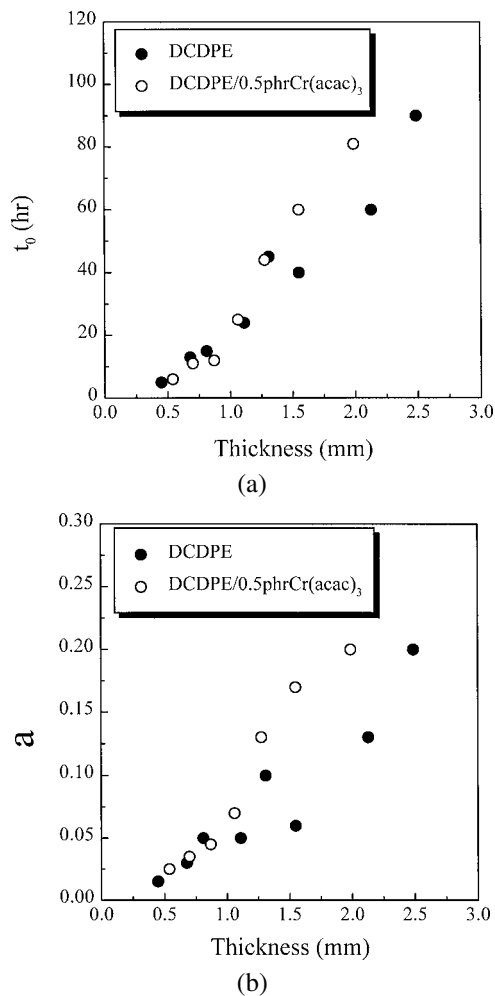


Figure 7. (a) ' t_0 ' and (b) ' a ' in Equation (5) chosen to fit the secondary stage of diffusion as a function of sample thickness for (●) DCDPE cyanate ester resins and (○) DCDPE incorporating 0.5 phr $\text{Cr}(\text{acac})_3$, during exposure to 60 °C/100%RH environment.

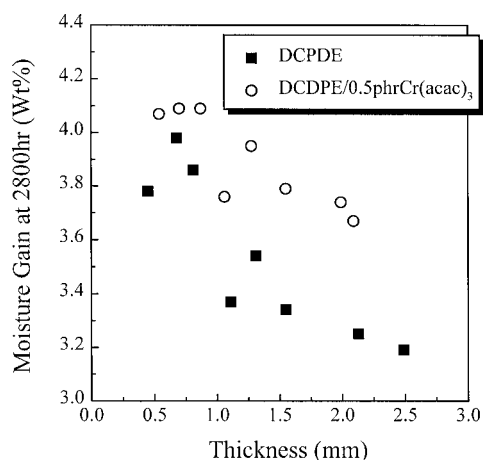


Figure 8. Moisture gain as a function of sample thickness for (●) DCDPE cyanate ester resins and (○) DCDPE incorporating 0.5 phr $\text{Cr}(\text{acac})_3$, after exposed to 60 °C/100%RH environment for 2800 h.

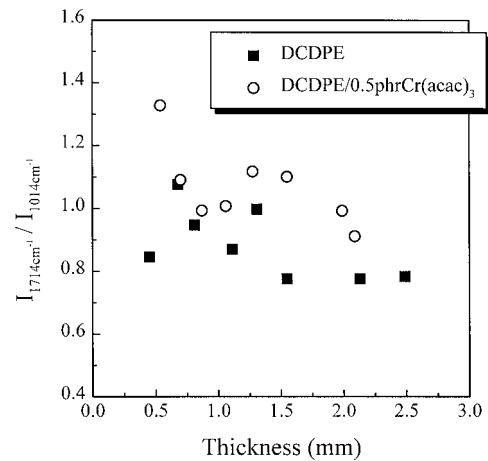


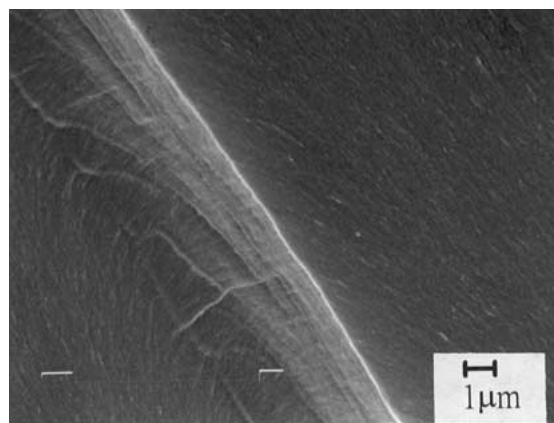
Figure 9. $I_{1714\text{cm}^{-1}}/I_{1014\text{cm}^{-1}}$ peak intensity ratio calculated from IR spectra of (●) DCDPE cyanate ester resins and (○) DCDPE incorporating 0.5 phr $\text{Cr}(\text{acac})_3$, after being exposed to 60 °C/100%RH environment for 2800 h and re-dried.

its addition to epoxy formulation was found to increase the moisture resistance of cured resins [9, 21, 22]. In this study, the incorporation of 0.5 phr $\text{Cr}(\text{acac})_3$ into DCDPE resin formulation was found to increase the density of cured resins substantially from 1.215 to 1.226. The diffusion coefficient D_x in the first-stage of moisture absorption was also smaller than that of the neat DCDPE resins, especially when the thickness was more than 1 mm (see Figure 6). Meanwhile, the estimated ' a ' and ' t_0 ' became larger, as shown in Figure 7. The smaller diffusion coefficient and lower deviation from the Fickian for $\text{Cr}(\text{acac})_3$ -containing specimens were believed to be due to the fact that its density is larger than that of the neat resins.

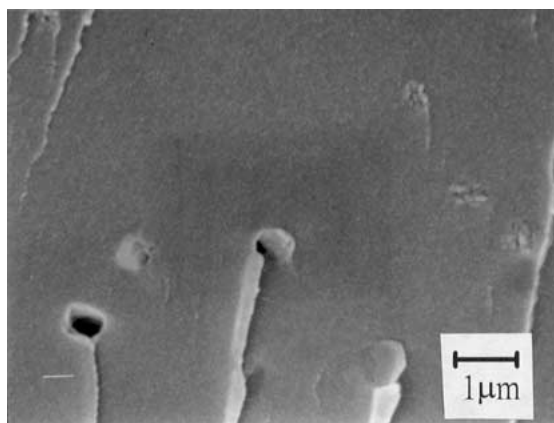
However, the moisture gain of the $\text{Cr}(\text{acac})_3$ -containing DCDPE resins exposed to a 60 °C/100%RH environment for 2800 h was larger than that of the neat resins of the same thickness (see Figure 8). The degree of hydrolysis defined by the intensity of carbonyl peaks in the IR spectra was also higher for the $\text{Cr}(\text{acac})_3$ -containing DCDPE resins after re-drying (see Figure 9). Apparently, $\text{Cr}(\text{acac})_3$ could accelerate the hydrolysis of DCDPE resins in the same manner as it accelerated the curing reactions. Figure 10 shows that the fracture surface of the re-dried DCDPE resin incorporating $\text{Cr}(\text{acac})_3$ contains voids of a size of $\sim 0.5 \mu\text{m}$, which were not found in the fracture surface of untreated samples or re-dried neat DCDPE resin (see Figure 4(b)). Thus, it is believed that the voids were formed in the regions where the $\text{Cr}(\text{acac})_3$ was locally concentrated. Once the voids formed, the moisture condensed inside. If the above specimens were rapidly heated to solder temperature ($\sim 200^\circ\text{C}$), the vaporized moisture inside the voids created high vapor pressure in the network, resulting in blistering, as reported in the literature [1]. To eliminate this problem, the specimens should be dried before soldering.

Conclusions

A two-stage moisture absorption behavior was found for the cured DCDPE resins. The first stage followed the Fickian



(a)



(b)

Figure 10. SEM micrographs of fracture surface of DCDPE resins incorporating 0.5 phr $\text{Cr}(\text{acac})_3$: (a) without moisture absorption and (b) after being exposed to 60 °C/100%RH environment for 2800 h and re-dried.

diffusion, whereas the secondary stage was a swelling-controlled diffusion. By assuming that the diffusion coefficient in the secondary stage decreased with time, as suggested by Equation (5), we were able to fit the experimental data agreeably until the specimens were substantially hydrolyzed. After that, the moisture absorption was further enhanced. The incorporated $\text{Cr}(\text{acac})_3$ could accelerate the hydrolysis of triazine rings in the cured networks, facilitating the formation of voids. Thus, to reduce the chance of

blistering, the limited use of metal complex accelerators in the cyanate ester formulations is suggested.

Acknowledgement

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