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# Moisture sorption–desorption–resorption characteristics and its effect on the mechanical behavior of the epoxy system

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## Abstract

Thermosetting epoxy resins are attractive materials for many engineering applications, as they are low in density, with excellent mechanical properties and easily fabricated by processes such as injection molding, extrusion and vacuum forming. However, the hostile hygrothermal environment can degrade the epoxy system. In this study, moisture sorption–desorption–resorption characteristics of the DGEBA/DDA epoxy system have been investigated by the hygrothermal aging and molecular dynamic (MD) simulation. Also, the effects of moisture on the mechanical behavior of the epoxy system have been studied by the uniaxial tensile test and a scanning electron microscopy (SEM), for the unaged, moisture saturated, completely desorbed and moisture re-saturated specimens, respectively. Results show that the moisture diffusion in epoxy system is not only dependent on the hygrothermal conditions, but also on the specimen thickness and hygrothermal history. Due to the effect of the hygrothermal aging, both the tensile elastic module and tensile strength of the studied epoxy system have been reduced, that is, the absorbed moisture has deleterious effects on the physical properties of epoxies and can, therefore, greatly compromise the performance of an epoxy-based component.

*Keywords:* Epoxy; Hygrothermal aging; Mechanical properties

## 1. Introduction

Thermosetting epoxy resins are widely used as adhesives, composites and laminates. This is because of its good thermal, chemical, physical, electrical, and mechanical properties, combined with satisfactory processing characteristics via short extrusion, injection molding cycles and excellent mold flow. Especially, they have wide applications in microelectronic packaging, such as the encapsulant and underfill agent in the mounting of chip assemblies to the printed circuit board.

However, in most applications the epoxy-based component has the potential of being exposed to a humid environment and susceptible to the moisture sorption. The capability of polymer materials to absorb moisture from the environment is one of the major reliability concerns for microelectronic devices encapsulated in plastic packages. The absorbed moisture has deleterious effects on the physical properties of epoxies and can, therefore, greatly compromise the performance of an epoxy-based component. Also, moisture condensation into microgaps (delaminations or cracks) between the die surface and molding compound (MC) can cause failures due to increased leakage currents, charge instabilities, or corrosion of aluminum metallization. Although many investigators have been concerned with the problems induced by moisture in recent years [1–7], the durability of the polymer is still need to be investigated in depth, particularly with regard to hygrothermal aging.

In this study, moisture sorption–desorption–resorption characteristics of DGEBA/DDA epoxy system have been investigated by the hygrothermal aging and molecular dynamic simulation. Here, resorption refers to the sorption process after a cycle of sorption and desorption. The effects of moisture on the mechanical behavior of the epoxy system have been studied by the uniaxial tensile test for the unaged, saturated (preconditioned under hygrothermal conditions, 85 °C/85%RH), completely desorbed (dry under thermal conditions, 85 °C) and re-saturated (re-preconditioned under hygrothermal conditions, 85 °C/85%RH) specimens, respectively. The tensile fracture surfaces have been observed by

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a scanning electron microscopy (SEM). Many significant results have been achieved.

## 2. Basic theories

### 2.1. Moisture diffusion theories

The most common approach to modeling moisture sorption is Fick's law applied to single free-phase diffusion. Fick's law predicts that the mass of water absorbed increases linearly with the square root of time, and then gradually slows until an equilibrium plateau, i.e. saturation, is reached. The moisture sorption by epoxy under hygrothermal conditions can generally be described by Fick's law [8]:

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D_x\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(D_y\frac{\partial C}{\partial y}\right)+\frac{\partial}{\partial z}\left(D_z\frac{\partial C}{\partial z}\right) \tag{1}$$

For the isotropic ($D_x=D_y=D_z=D$) material,

$$\frac{\partial C}{\partial t}=D\left(\frac{\partial^2 C}{\partial x^2}+\frac{\partial^2 C}{\partial y^2}+\frac{\partial^2 C}{\partial z^2}\right) \tag{2}$$

For the large plane sheet sample, the moisture sorption process can be considered as one-dimension, and then Fick's equation can be simplified as,

$$\frac{\partial C}{\partial t}=D\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{3}$$

where $D$ is the diffusion coefficient, $C$ is the concentration of the diffusing substance, $t$ is the time, $x$, $y$ and $z$ are the axes along the concentration gradient, as shown in Fig. 1. For a plate sheet specimen of thickness $h$, the initial and boundary conditions are that both surfaces of the plate sheet are assumed to be at constant concentration $C_\mathrm{i}$, while initial uniform concentration $C_0$ within the plane sheet, $-h/2<x<h/2$. And the initial and boundary conditions can be expressed as:

$$C=\begin{cases} C_\mathrm{i} & x=-h/2,\quad x=h/2,\quad t\geq 0 \\ C_0 & -h/2<x<h/2,\quad t=0 \end{cases} \tag{4}$$

The simple moisture diffusion process, in which the chemical reactions between polymer molecular and water molecular are not considered, can be described by Fick's second law Eq. (1). Upon solving Fick's diffusion equation using the method of separation of variables, the concentration distribution can be derived as [8].

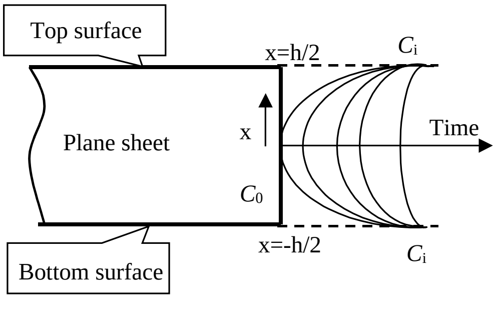

Fig. 1. Initial/boundary conditions and concentration change with time.

$$\frac{C(t,x)-C_0}{C_\mathrm{i}-C_0}=1-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\exp\left\{-\frac{(2n+1)^2\pi^2 D}{h^2}t\right\}\times\cos\frac{(2n+1)\pi}{h}x \tag{5}$$

where $C(t,x)$ is the concentration of moisture at distance $x$ and time $t$. Generally, the initial uniform moisture concentration within the specimens can be treated as zero, $C_0=0$. Then the total amount of moisture $M_t$ that ingress the epoxy-based specimen at time $t$ is given by

$$M_t=\int_{-h/2}^{h/2}(C-C_0)\mathrm{d}x=\int_{-h/2}^{h/2}C\mathrm{d}x \tag{6}$$

Integrating above equation and the following expression can be derived:

$$\frac{M_t}{M_\infty}=1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{-\frac{(2n+1)^2\pi^2 D}{h^2}t\right\} \tag{7}$$

in which $M_\infty$ is the equilibrium moisture gain in the specimen after infinite exposure time. In order to investigate expediently, the initial weight of the unaged specimen $M_d$ is introduced, and then the analytical solutions for moisture diffusion can be expressed as

$$\frac{M_t}{M_d}=\frac{M_s}{M_d}\times\left(1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2\pi^2 D}{h^2}t\right)\right) \tag{8}$$

For the hygrothremal aging experiments, if the specimens are weighed periodically using thermal gravimetric technique to determine the percent weight change, thus, moisture uptake. The moisture uptake percentage, is determined from the equation:

$$\text{Moisture Uptake\%}=\frac{M_t}{M_d}\times 100\% \tag{9}$$

where $M_t$ is the total amount of moisture content absorbed by the epoxy-based sample at time $t$, $M_d$ is the original weight of the unaged specimen. The diffusivity, $D$, was determined from the slope ($K$) of the initial linear region of the plot of the percentage moisture uptake $M_t/M_d$ versus $\sqrt{t}$ curve [9],

$$D=\frac{\pi}{16}\left(\frac{h}{M_\infty/M_d}\right)^2 K^2 \tag{10}$$

where $h$ is the thickness of the specimen, $t$ is exposure time and $M_\infty$ is the maximum moisture gain (saturation).

### 2.2. Molecular dynamic simulation

Molecular dynamics (MD) simulation techniques are playing an important role in modern characterization of polymers. These techniques are likely to benefit the study of polymers by increasing the understanding of chemical and physical processes at the molecular and atomic level. Over the last 15 years detailed atomistic molecular modeling techniques on the basis of classical molecular mechanics have become a widely used method for the investigation of the sorption and diffusion of small molecules in the amorphous polymers or penetrate through the membrane materials based on these materials [10–17].

In this study, MD method is employed for simulation of moisture diffusion in the studied epoxy system. Diffusion coefficients can be obtained from the time dependence of the average mean squared displacements (MSD) of mass, using the Einstein relation as follows:

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\sum_{1}^{n}\left\langle\left[R_i(0)-R_i(t)\right]^2\right\rangle \quad (11)$$

where $t$ is the simulation time, $R_i$ is the position of the particle center of mass, $n$ is the number of particles of a given type, and the angle brackets denote averaging over all choices of time origin. This quantity is calculated directly from the MD trajectory over a long time period (usually more than 1 ns). Therefore, diffusion coefficients are calculated directly from the slope of the MSD versus time curves obtained from the MD simulation for a relatively long time.

In this work, the initial microstructure of the epoxy system containing four molecules of water was generated by means of the ‘amorphous cell’ module in the Materials Studio software (Version3.0) designed by Accelrys Inc., San Diego, CA, USA [18]. The generation of an initial polymer microstructure was based on the ‘self-avoiding’ random-walk method of Theodorou and Suter [19]. Periodic boundary conditions are imposed on the cubic unit cell in order to eliminate surface effects. The cubic unit cell is visualized as being surrounded on all sides by replicas of itself, thus forming an infinite three-dimensional microlattice. The amorphous cell structure of studied epoxy system with four molecules of water inserted is shown in Fig. 2. The length of the sides of the cubic unit cells in this study was 20–22 Å. In this amorphous cell model, there are 1018 atoms including four molecules of water.

After the initial microstructure is generated, the next step is the calculation and minimization of the potential energy of the water–epoxy system. All interactions between the atoms of the polymer chains, between polymer chains and diffusing penetrant molecules (water molecules), and between the penetrant molecules themselves must be taken into account. This was accomplished by means of the discover module in the Materials Studio software [18]. All interaction potentials were simulated by means of the ‘PCFF’ forcefield improved from the ‘CFF91’ forcefield. This ‘forcefield’ describes the potential energy functions for all the different types of interactions involved in the diffusion of small penetrant molecules in a polymer matrix (bond stretching, bond angle bending, bond rotation, non-bonded van der Waals interactions, etc.).

Then, the NPT and NVE MD simulations were performed for the constructed and minimized epoxy network system at 85 °C. For the NPT ensemble, the number of molecules $N$, pressure $P$ and the temperature $T$ of the system are kept constant, whereas for the NVE ensemble, the number of molecules $N$, volume $V$ and energy $E$ of the studied epoxy system are kept constant. MD calculations simulate the natural motions of all atoms in a polymer system over time at non-zero temperature and the MD algorithm makes use of Newton’s equation of motion; thus giving a complete dynamic description of the polymeric material. The number of steps of NPT MD simulations was 2,000,000 (2 ns), and the output frequency was every 2000 steps. The time step of 1 fs ($1\times 10^{-15}$ s) is taken to be constant for all the simulations of this study. There are seldom reports about MD simulations of the epoxy network system, because this kind of simulation is rather complex compared to that of the linear polymers investigated by many researchers. The detailed simulation methodology will be specially reported.

## 3. Experiments

The epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA) cured with dicyandiamide (DDA) hardener, which are commonly used as the adhesive. The detailed structures of the resin and crosslinker molecules are shown in Fig. 3. The moisture uptake performance of studied epoxy system was determined using thin film bulk adhesive specimens, which were made by injection molding. In order to

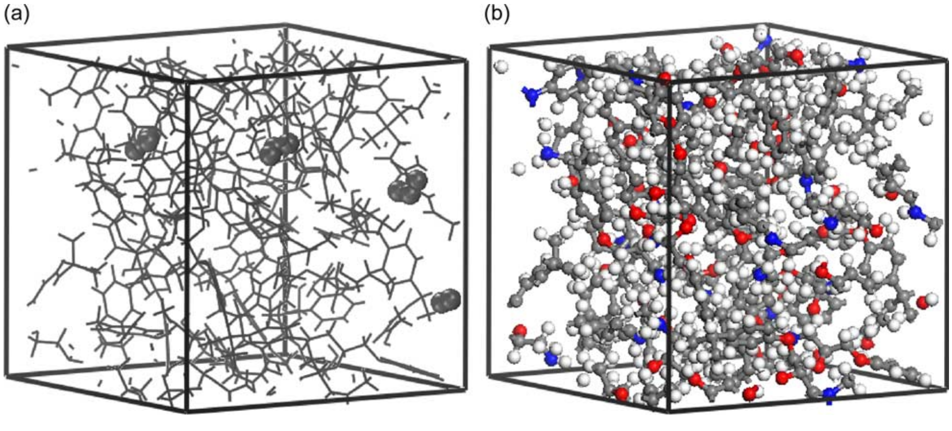

Fig. 2. Amorphous cell structure of studied epoxy system with four molecules of water inserted.

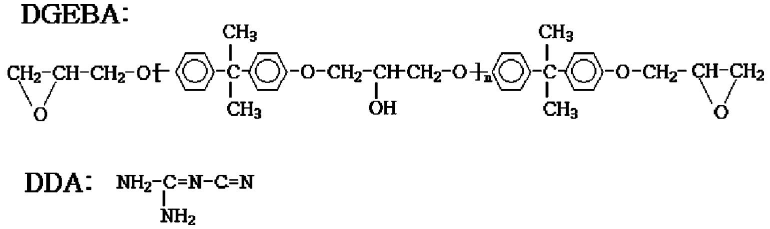

Fig. 3. Structure of the resin and crosslinker molecules: diglycidyl ether of bisphenol A (DGEBA) and dicyandiamide (DDA).

combine gravimetric and tensile testing, 'dog-bone' specimens were made with different thickness (1.2, 1.5, 2.0, 2.5 mm). Specimen geometry and dimensions used in this study are shown in Fig. 4. The specimen sizes resulted in a suitably large surface area to thickness ratio, ensuring that the diffusion process was essentially one-dimensional. The completed 'dog-bone' specimens were kept in a desiccator for a minimum of 10 days prior to exposure. Five adhesive specimens for every thickness were made. In order to investigate the effects of the moisture on the mechanical behavior of the epoxy system, another 20 adhesive specimens for the thickness of 3 mm were made for the uniaxial tensile test and these specimens were divided into four groups, that is, unaged, saturated, desorbed and re-saturated groups, respectively.

### *3.1. Moisture sorption–desorption–resorption experiments*

In order to investigate the moisture sorption–desorption–resorption characteristics, three main experimental steps are carried out. Firstly, the completely dry/unaged specimens were sent into the hygrothermostat and preconditioned under the hygrothermal conditions, 85 °C/85%RH, until the weights of the specimens remained constant, that is, the specimens reached saturation. Then, some saturated specimens were dried in vacuum drying oven with thermal conditions, 85 °C. Finally, some completely-dried samples were subjected to resorption under the same hygrothermal conditions, 85 °C/85%RH. During the moisture sorption–desorption–resorption experiments, the specimens were weighed periodically using thermal gravimetric technique to determine the percent weight change, thus, moisture uptake.

### *3.2. Tensile tests and fracture surfaces observation*

Hygrothermal aging refers to the process in which the deterioration of the mechanical performance and integrity of composites materials results from the combined action of moisture and temperature. In order to investigate the effects of the hygrothermal aging on the mechanical behavior of the epoxy system, the uniaxial tensile tests have been carried out for the unaged, saturated, desorbed and re-saturated specimens, respectively. These tests were performed on a mechanically driven test machine with 10 kN of capacity at room temperature (20–25 °C) and a crosshead speed of 1 mm/min. An extensometer was placed in the narrow section of the dumbbell specimens to record the extension of the specimen with applied loading. The tensile stresses in the dumbbell specimens were calculated by dividing the applied load by the original cross-sectional area. It was assumed that the change in cross-sectional area of the specimen during deformation was insignificant. Any specimens that failed outside the neck section were discarded. Because the studied epoxy system is a brittle material, the relation between stress and strain are linear, except that a very small plastic strain appeared just before fracture. Therefore, the tensile elastic module can be easily obtained.

Fracture surface morphology analysis, using scanning electron microscopy (SEM), is one of important methods to study the material fracture mechanism [20,21]. In this work, the fracture surfaces of the tensile specimens were analyzed by scanning electron microscopy (XL Series: XL30ESEM), using secondary electrons with the electron beam voltage ranging between 15 and 20 kV. The samples were mounted and sputter-coated with a platinum–gold using a Polaron sputter coater. For the saturated and re-saturated cases, the samples were not dried or treated in any other way before coating and viewing.

## 4. Results and discussion

### *4.1. Moisture sorption–desorption–resorption characteristics*

The moisture sorption profiles of the specimens with different thickness, under hygrothermal conditions 85 °C/85%RH, are compared in Fig. 5. The different symbols represent experimental data and each of the data points shown is the average value obtained from every group experimental results. The slope ($K$) of the initial linear region of the plot (Fig. 5), the maximum moisture gain ($M_\infty$) and the original weight of the unaged specimen ($M_d$) can be directly obtained from the experimental results, so the diffusivity ($D$) is calculated according to Eq. (10). Then, substituting the calculated diffusivity into Eq. (8) and assuming one finite maximal value of $n$(100,000), the analytical solution curve (the bold curve, shown in Fig. 5) can be calculated by mathematic software MATLAB. From Fig. 5, it can be easily seen that the

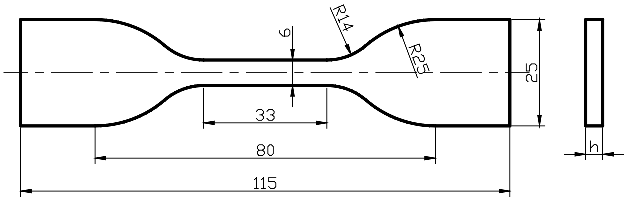

Fig. 4. Dimensions of an adhesive dumbbell specimen according to ASTM D 638M-84 (all dimensions are in mm).

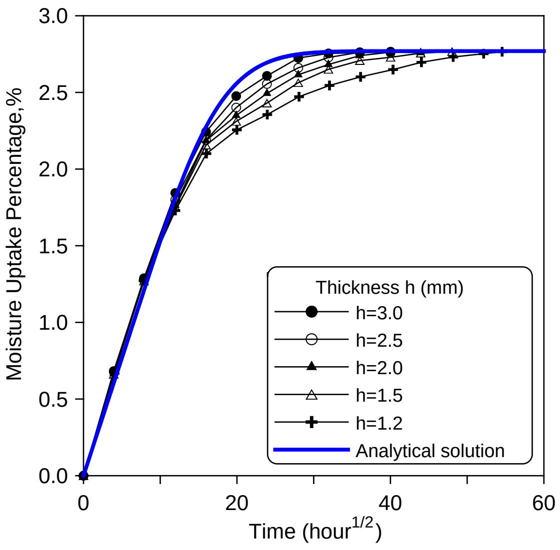

Fig. 5. Moisture uptake percentage of experimental samples with different thickness at 85 °C/85%RH. The symbols are experimental data and the bold line is the analytical solutions.

uptake initially increases linearly with respect to $\sqrt{\text{time}}$ $\left(\sqrt{\text{hour}}\right)$ and then levels off, in spite of the diversities of the specimen thickness. That is, there is two-stage moisture absorption behavior for the studied epoxy system. The first stage followed the Fickian diffusion, whereas the secondary stage was another different diffusion in that the diffusion coefficient was decreased with time. Since the length and width of the specimens are much larger than the thickness, diffusion through the edges is negligible and the moisture diffusion can be treated as a one-dimensional process. Also, it is obvious that the slopes of the initial linear regions of the sorption curves and the equilibrium moisture uptake are almost same for all specimens with different thickness. In the initial linear regions, the excellent agreement between the analytical solutions and the experiments supports the deduction that the diffusivity is a constant and moisture diffusion is Fickian at low moisture content. Also, the two-stage absorption behavior became less discernible with the increase of the sample thickness. However, non-Fickian diffusion behavior becomes more and more obvious as the moisture concentration increases.

Fig. 6 shows the moisture sorption–desorption–resorption characteristics of the specimens with thickness of 2 mm. In this figure, the different symbols represent experimental data. For all the cases, the uptake initially increases linearly with respect to $\sqrt{\text{time}}$ and then levels off, which is similar to the above-reported results. The analytical curves are constructed from the above-mentioned data processing, and compared with the experimental data of three processes in Fig. 6(b). It can be easily seen that both desorption and resorption are faster than sorption. Also, the differences between the experimental data and analytical curves decrease with hygrothermal history, that is, the two-stage absorption behavior became less discernible with hygrothermal cycling. The fact that resorption is faster than sorption clearly demonstrates that there is a change of material properties after a cycle of sorption and desorption. Additionally, it should be noted that not only the resorption process is faster than the sorption process, but also the equilibrium water content of the resorption process (moisture uptake percentage, 2.799%) is larger than that of the sorption process (moisture uptake percentage, 2.751%). Generally speaking, the increasing of the free volume in the polymer matrix will strengthen the solubility of the gas in the polymer matrix, and it has been actually reported that the penetration of the moisture into the polymer will increase the free volume by the swelling effect [22]. In this study, the moisture sorption, desorption and the resorption process would increase the free volume of the epoxy system. So, the equilibrium water content will increase with hygrothermal aging.

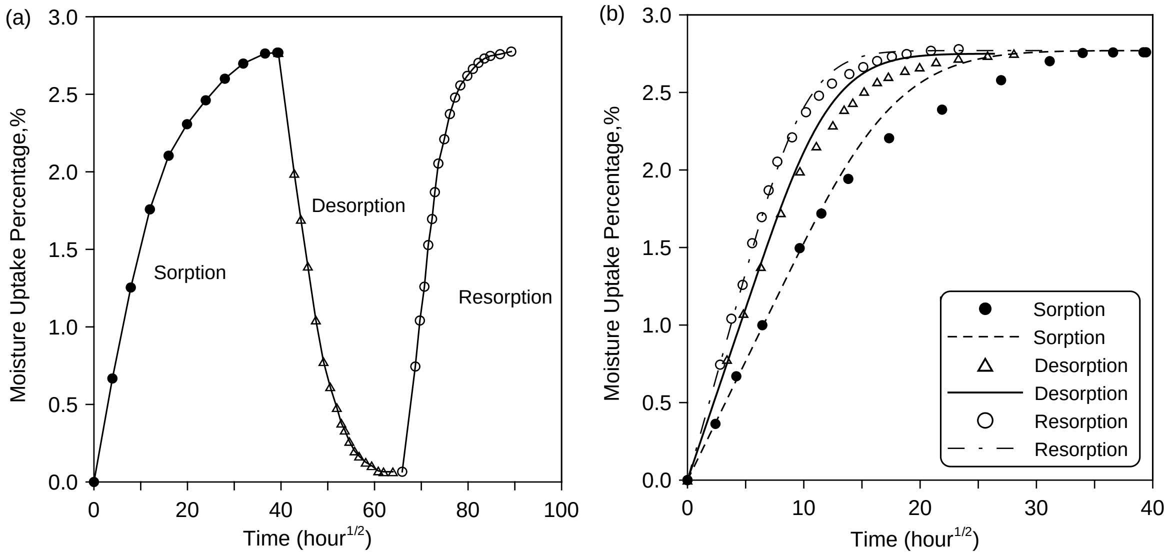

Fig. 6. Moisture sorption–desorption–resorption characteristics curves. (a) Experimental results; (b) experimental and analytical solutions: the symbols are experimental data and the curves are the analytical solutions.

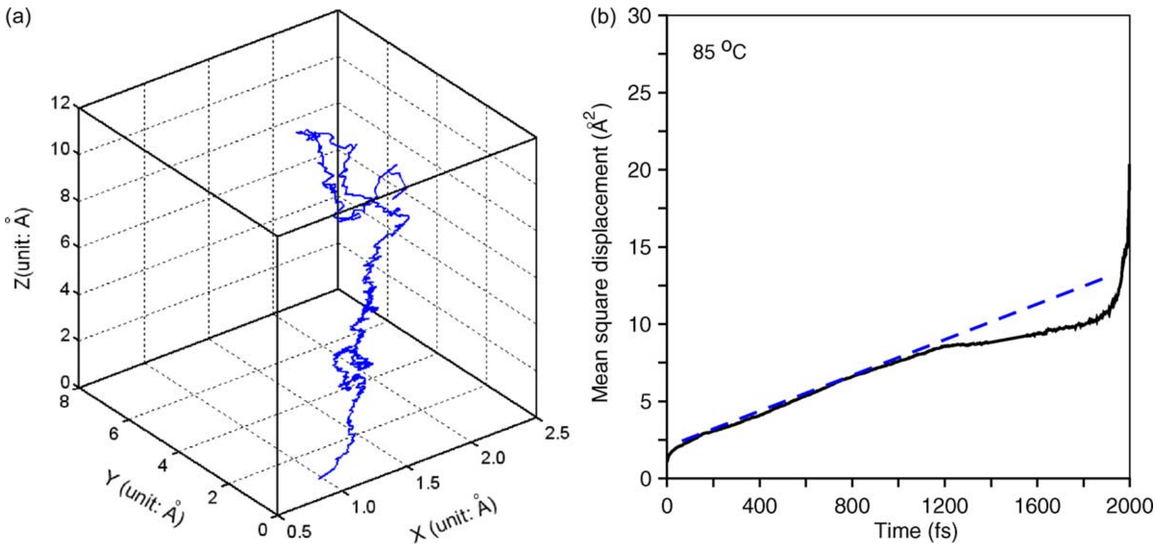

Fig. 7. MD simulation results: (a) Trajectory of a $H_2O$ molecule in the studied epoxy system during a period of 2 ns. (b) Mean-square displacements of $H_2O$ molecules in the studied epoxy system.

Fig. 7 shows the average mean squared displacements (MSD) plot of four water molecules and the trajectory of a $H_2O$ molecule in the studied epoxy system during a period of 2 ns. They follow a general trend observable in glassy polymers [10–17]. It is obvious that the plots of MSD versus time are indeed linear over a period of time of about 1.5 ns. At longer times, however, the plots deviate from linearity due to the increasing statistical error involved in the calculations of MSD.

The moisture diffusion coefficients from experiments and molecular dynamics (MD) simulations can be determined from the slopes of the initial linear regions of Figs. 6 and 7, according to Eqs. (10) and (11), respectively. The comparison between the moisture diffusion coefficients from experiments and MD simulations are shown in Fig. 8. It can be seen from Fig. 8 that the moisture diffusion coefficient from MD simulations is much more close to that of sorption process than the desorption and resorption cases. This result, to some extent, indicates that there is a change of material properties (e.g. molecular structures) after a cycle of sorption and desorption process, which will be further discussed in the following.

Also, judging these results is to be noticed that there are some possible errors of experimental and simulation results. However, the deviations between the experimental and MD simulations results are not considerably greater than a factor of about three. It is well know that the causes of error between the experimental and MD simulation results are extensive. For the experiments, it is difficult to obtain really amorphous polymeric materials because the crosslinking reactions of the epoxy system are dependent many factors, such as the quantity of the different components, temperature, time, and so on. On the other hand, for the MD simulation, there are several assumptions used in the idealized models of studied epoxy system and limited simulation time. Also, the errors form the basic statistical mechanics of the MD simulation are inevitably. It is, therefore, generally accepted that a coincidence between measured and simulated diffusivity and solubility values within a factor of 3–5 is still acceptable [12,17]. Therefore, in the given case, the investigated epoxy system can be considered to be reasonably equilibrated at least as far as the correct representation of transport properties is concerned.

Therefore, the moisture diffusion in epoxy system is not only dependent on the hygrothermal conditions, but also on the specimen thickness and the hygrothermal history [7,8]. For the latter, it can be understood by following the course of molecular relaxation of the polymer network. Because the penetrant molecules (water molecules) diffuse into the polymers, there are some changes in all interactions between the atoms of the polymer chains, between polymer chains and diffusing water molecules, and between the penetrant molecules themselves. So, a glassy polymer has to change its

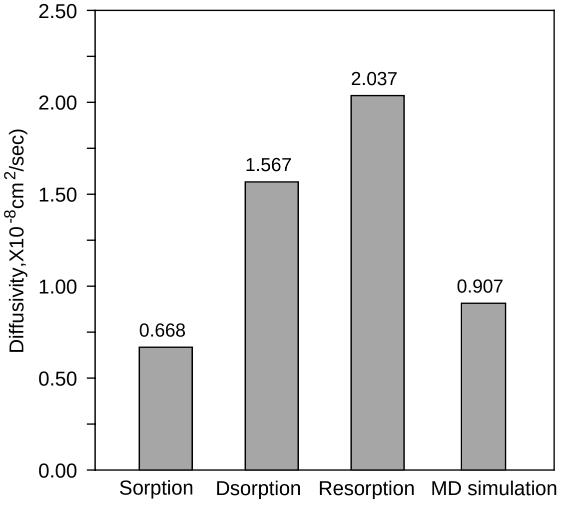

Fig. 8. Moisture diffusivity for moisture sorption–desorption–resorption.

molecular structure to conform to the presence of the penetrant in a sorption process. The change of molecular structure from one conformation to another is a time dependent phenomenon that may be considered a relaxation process characterized by a spectrum of relaxation times. Dependent on how the polymer network is disturbed by the penetrant, two classes of sorption behavior may be observed.

One is Fickian diffusion. The polymer network may only make minor changes of molecular structure to reach equilibrium for a small disturbance, such as low moisture concentration or temperature. Then, very short relaxation times may be enough to complete the local molecular motions and Fickian diffusion always prevails because the time scale of molecular arrangement is much shorter than that of diffusion. In contrast, there is another diffusion behavior, non-Fickian diffusion. In this case, the polymer network may be severely disturbed by the outside disturbance, such as high moisture concentration and temperature. So, the large adjustments of segmental conformations may be underwent in order to reach equilibrium again, that is, the chain segments may have to travel over longer distances which are characterized by long relaxation times. If the time rate of change of concentration in a volume element is large, then the polymer network may not be able to reach conformations in equilibrium with the presence of the penetrant at every concentration in the sorption process. Thus, the mass transport process would not be free from viscoelastic effects and non-Fickian diffusion takes place.

For a sorption experiment conducted on specimens of different thickness, at a given fractional distance through the sheet, the concentration changes more slowly in thicker specimens. Thus, the thicker the specimen, the more time is provided for molecular rearrangement of the polymer network. Therefore, Fickian diffusion behavior may be more obvious for the thicker specimens. In contrast, the polymer network would not have enough time for long-range molecular motions for the thinner specimens, and then the non-Fickian diffusion behavior may be more obvious.

After desorption, the polymer would exhibit a network structure with ‘frozen in’ segmental conformations. The resorption process would thus be different from the sorption process because after a cycle of sorption and desorption, the network structure has already been modified. A sorption–desorption cycle can effectively increase the preexisting free volume of the resin and render the subsequent sorption process different from and fast than the original. Additionally, Fourier transform infrared spectroscopy (FTIR) is one powerful tool to study the effect of hygrothermal aging on the change of the molecular conformation of epoxy resin, or reaction kinetics study of synthesis and characterization [23–26]. It is thought that most polymer material will undergo chemical hydrolysis under hygrothermal environments. After hygrothermal condition test and FTIR analysis, an increase in hydroxyl group (3450 $\text{cm}^{-1}$), alkyl group (2930 $\text{cm}^{-1}$), and carbonyl group (1655 $\text{cm}^{-1}$) together with a corresponding drop in ester peak (1728 $\text{cm}^{-1}$) can be used to further verify the contention that the material is undergoing chemical hydrolysis with increased hygrothermal aging.

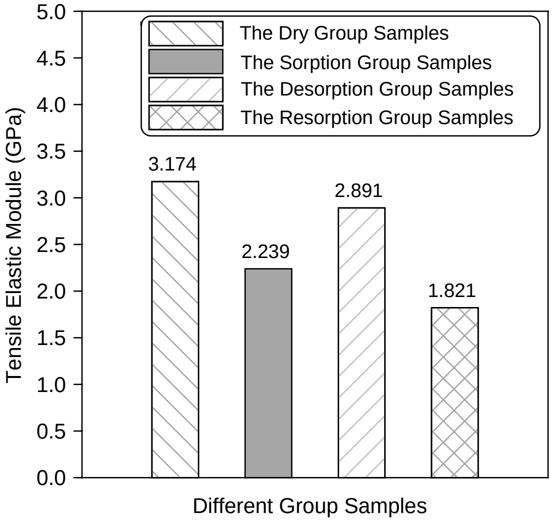

Fig. 9. Effects of hygrothermal aging on the tensile elastic module of the epoxy system.

### 4.2. Effect of moisture on mechanical properties of the studied epoxy system

In this section, the uniaxial tensile tests have been carried out for the unaged, saturated, desorbed and re-saturated specimen, respectively, in order to investigate the effects of the hygrothermal aging on the mechanical behavior of the epoxy system and verify the alteration of the epoxy network after the sorption and desorption processes.

Fig. 9 shows that the effects of hygrothermal aging on the tensile elastic module of the studied epoxy system. Each of the data points shown is the average value obtained from every group experimental results. For the elastic module, standard deviations of the unaged, saturated, desorbed and re-saturated group samples are 0.0983, 0.0475, 0.0536 and 0.0357 GPa, respectively. Also, it can be calculated that the reduction of the elastic modules of the unaged, saturated, desorbed and

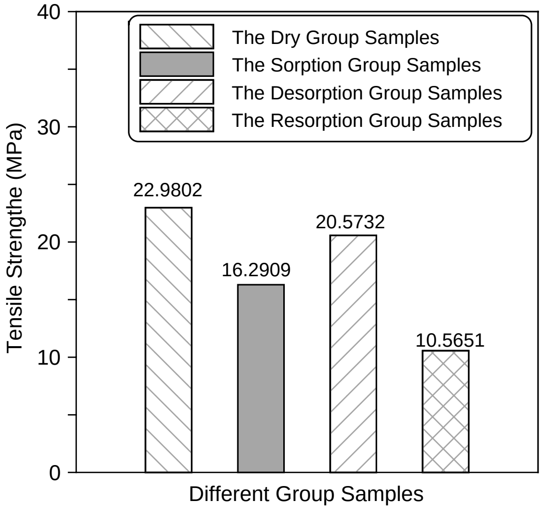

Fig. 10. Effects of moisture on the tensile strength of the epoxy system.

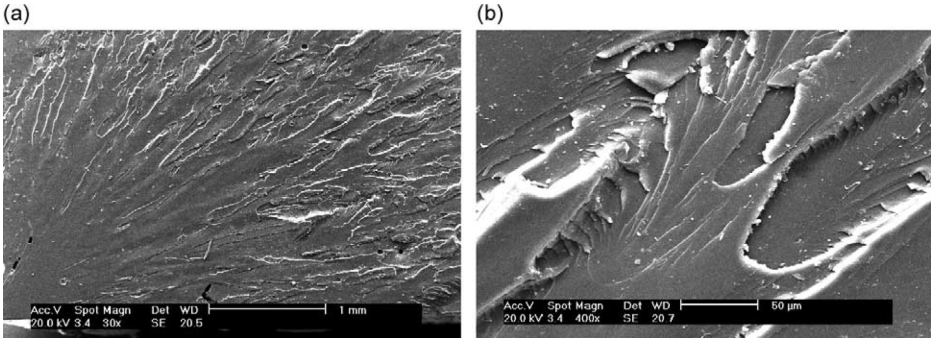

Fig. 11. SEM micrographs of the fracture surface of unaged specimens: (a) the fracture surface (×30); (b) higher magnification of the features in the rapid crack growth zone (×400).

re-saturated group samples are 29.45, 8.920 and 41.50%, respectively, compared to the unaged group samples. The effects of hygrothermal aging on the tensile strength of the studied epoxy system are shown in Fig. 10. Standard deviations of the unaged, saturated, desorbed and re-saturated group samples are 1.4967, 1.2772, 2.3319 and 1.7351 MPa, respectively. Due to the effect of the hygrothermal condition, the tensile strength of the unaged, saturated, desorbed and re-saturated group samples are also reduced much, compared to the original unaged group samples. This probably arises because of the plasticization effect of absorbed moisture. The extent of this plasticization process seems to increase markedly with hygrothermal history, except there is slightly shifted back of elastic module for the desorbed samples.

According to the analysis in Section 4.2, the polymer would exhibit a network structure with ‘frozen in’ segmental conformations and the preexisting free volume of the resin can be effectively increased after a cycle of sorption and desorption. Also, the effect of hygrothermal aging on the glass transition temperature ($T_g$) is another focus and investigated by some researchers [27,28]. It is known that, in the epoxy resin, the glass transition temperature can be related to the crosslinked density. With a decrease of crosslink density, the glass transition shifts to a lower temperature. Their experimental results show that irreversible hygrothermal aging decreases the $T_g$ of DGEBA/DDA by about 20 °C. In other words, the hygrothermal aging has damaged the epoxy system.

### 4.3. Fracture surfaces fractographic analysis

In order to know the effect of the moisture on the fracture mechanisms, fractographic analysis of the fracture surfaces are performed by SEM for the unaged, saturated and completely desorbed specimens. A considerable amount of information has been reported on the appearance of fracture surfaces formed by crack propagation in glassy polymers [29,30], by scanning electron microscopy (SEM). It is found that there are several distinct patterns on fracture surfaces, such as radial striations, regularly spaced ‘rib’ markings, irregular ‘mackerel’ or ‘patch’ and parabolic shape patterns.

The SEM micrographs of the fracture surface of the unaged, saturated and completely desorbed specimens are shown in Figs. 11–13, respectively. It is well known that there are one slow crack growth zone (near crack initiation point) at the beginning of the crack growth and one rapid crack growth zone (away from crack initiate-point) when the instability criterion for crack growth is met with the continually increased loading. In order to express well, the SEM micrographs with the overall fracture surface and the rapid crack growth zones are respectively given in different magnification.

From Fig. 11, there is firstly some relatively smooth fracture surface in the slow crack growth zone and then spaced ‘rib’ markings perpendicular to the direction of crack growth appeared in the crack speeding zones. With the crack growing, the distinct conic-shaped patterns appeared in the rapid crack growth zone.

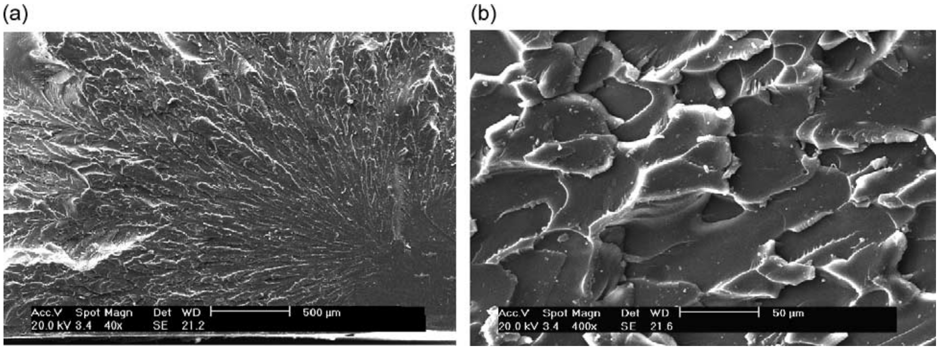

Fig. 12. SEM micrographs of the fracture surface of saturated specimens under 85 °C/85%RH: (a) the fracture surface (×30); (b) higher magnification of the features in the rapid crack growth zone (×400).

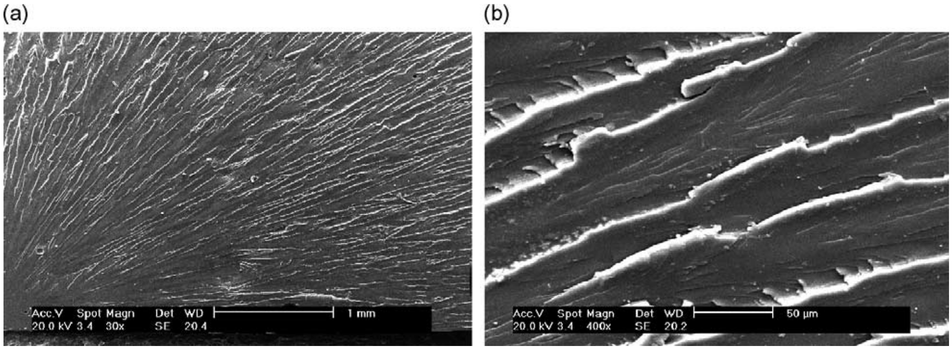

Fig. 13. SEM micrographs of the fracture surface of completely desorbed specimens under thermal conditions, 85 °C: (a) the fracture surface (×30); (b) higher magnification of the features in the rapid crack growth zone (×400).

For the saturated specimens which are precondition under hygrothermal conditions, 85 °C/85%RH, it can be seen from Fig. 12 that narrowband (narrow shear band) appears firstly in the slow crack growth zone. However, irregular 'mackerel' or 'patch' patterns are found on fracture surfaces in the rapidly moving crack zones. This fracture surface patterns shows that, during the continuous loading, the crazes grow and simultaneously the crack propagates slowly, their fronts intersect each other and form the parabola patterns which may be very flat like straight lines. When the instability criterion for crack growth is met, the crack propagates at a very high speed and the crazes initiated near the crack front have no enough time to grow. Thus, a large number of fine near circle or ellipse patterns are left on the fracture surface.

Fig. 13 shows that crack growth takes place by breakdown of the craze along its midrib, which leaves a relatively smooth fracture surface and dissipates relatively small amount of energy to create new surfaces in the slow crack growth zone. While rapid crack growth zone, the crack growth speeds up with the continuous loading and the fracture surfaces have regularly spaced 'rib' markings perpendicular to the direction of crack growth, which appears to be related to a type of stick/slip propagation due to either crack bifurcation or the effect of stress waves. The transition between these two distinct types of surface morphology can be very abrupt. Compared to the Fig. 11 of the unaged samples, there are no distinct conic-shaped patterns in the fracture surface of desorbed specimens under thermal conditions, 85 °C; furthermore, it can be seen that the spaced 'rib' markings are more regular, fine and narrow from the SEM micrographs with same magnification. It means that the desorbed epoxy specimens become more brittle than the unaged ones, when the specimens are preconditioned under the hygrothermal conditions and then desorbed.

Fractographic analysis results show that there is a transition from brittle to ductile between the dry and moisture-saturated specimens; while the transition from ductile to brittle between the saturated and desorbed specimens. This is because a low-molecular-weight molecule (water) may act as a diluent or plasticizer when it is incorporated into a polymer network, and the plasticization of epoxy resins is of particular importance since it may lead to serious degradation of bulk properties during environmental exposure, particularly at elevated temperatures [31]. On the other hand, this transition can be generally considered as being due to a competition between a brittle fracture mechanism such as crazing and a ductile mechanism such as bulk shear yielding. The ductile mechanism becomes more obvious than the unaged specimens because of the moisture-induced plasticization. So, the absorbed moisture has deleterious effects on the physical properties of epoxies and changed the fracture mechanisms.

## 5. Conclusions

In this study, moisture sorption–desorption–resorption characteristics of the DGEBA/DDA epoxy system have been investigated by the hygrothermal aging and molecular dynamic (MD) simulations. The effects of the moisture on the mechanical behavior of the epoxy system have been studied by the uniaxial tensile test and a scanning electron microscopy (SEM). It can be concluded that: (1) the moisture diffusion coefficients of the epoxy system are independent on the thickness of the specimen and the non-Fickian diffusion behavior becomes less discernible with the specimen thickness increasing. (2) Desorption and resorption processes are faster than sorption process, and resorption is the most fast among three cases. (3) MD simulation methodology plays an important role in improving the characterization of polymers and assisting in the verifying the experimental results. (4) Due to the effect of the hygrothermal aging, both the tensile elastic module and tensile strength of the studied epoxy system have been reduced, that is, the physical properties have been damaged. (5) Fractographic analysis results show that the absorbed moisture can change the fracture mechanisms of the polymer, and there is an evidence of the transition from brittle to ductile for the unaged and saturated specimens; while the transition from ductile to brittle for the saturated and desorbed specimens.

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