Thermal Properties and Water Sorption Behaviors of Epoxy and Bismaleimide Composites

Jongchul Seo, Wonbong Jang, and Haksoo Han*

Department of Chemical Engineering, Yonsei University, Seoul 120-749, Korea

Abstract: In this work, we prepared epoxy/BMI composites by using N,N'-bismaleimide-4,4′-diphenylmethane (BMI), epoxy resin (diglycidyl ether of bisphenol-A (DGEBA)), and 4,4′-diamino diphenyl methane (DDM). The thermal properties and water sorption behaviors of the epoxy and BMI composites were investigated. For the epoxy/BMI composites, the glass transition and decomposition temperatures both increased with increasing BMI addition, which indicates the effect of BMI addition on improved thermal stability. The water sorption behaviors were gravimetrically measured as a function of humidity, temperature, and composition. The diffusion coefficient and water uptake decreased and the activation energy for water diffusion increased with increasing BMI content, indicating that the water sorption in epoxy resin, which causes reliability problems in electronic devices, can be diminished by BMI addition. The water sorption behaviors in the epoxy/BMI composites were interpreted in terms of their chemical and morphological structures.

Keywords: epoxy/BMI composite, water sorption, thermal properties, morphological structure.

Introduction

As surface mounting devices have been developed as a main packaging type, more heat resistant and hydrolytic stable properties have been required for epoxy molding compounds or films for encapsulation material. Epoxy resins are widely used in industry, especially electronics, due to the advantages of heat resistance, high insulating properties, low dielectric constants, economical cost, and so on.[1-4] However, the performances of epoxy resin are limited by the considerable amount of moisture absorbed at equilibrium.[5-10] The presence of water in a polymer (*e.g.* epoxy resin) can lead to marked changes in the resin chemical and physical state. Absorbed moisture causes plasticization, induces differential swelling stresses, lowers the glass transition temperature (by as much as 20 °C), diminishes their mechanical strength, and generally degrades the physical properties. Therefore, it needs to minimize the water sorption in epoxy resin for performance of electronic devices.

To overcome the considerable amount of water sorption in epoxy resins, a promising approach has recently emerged, which consists in the formulation of thermoset/thermoset blends.[11,12] These systems generally belong to the class of inter-crosslinked or interpenetrating polymer networks. Owing to their peculiar molecular structure, these complex networks often exhibit synergistic effects, which produce considerable and unexpected improvements in some properties with respect to those of the neat components.

Bismaleimides have high crosslinking ability, high glass transition temperature, high thermal stability, and they absorb little water. Hence, in the present investigation an attempt was made to improve both the thermal stability and water sorption behaviors of epoxy resin using bismaleimide.

Generally, the chemical structure and microstructure (or morphological structure) of polymer films are two parameters that strongly influence the level of absorbed water and its rate of diffusion through the polymer composites.[5-10] The water sorption behaviors of the epoxy/BMI composites have been investigated by a gravimetrical method and interpreted by chemical and morphological structures.

Experimental

Materials. Epoxy/BMI composite films were prepared using three commercial sources; crosslinkable monomer N,N'-bismaleimide-4,4′-diphenylmethane (BMI, Aldrich Chemical Co.), epoxy resin diglycidyl ether of bisphenol-A (DGEBA, Shell Chemical Co.), and aromatic amine hardener 4,4′-diamino diphenyl methane (DDM, Aldrich Chemical Co). The chemical structures of these components are presented in Figure 1.

The compositions of the epoxy/BMI composites are

*Corresponding Author. E-mail: hshan@yonsei.ac.kr

(a) DGEBA: diglycidyl ether of bisphenol A

(b) DDM: 4,4′-diamino diphenyl methane

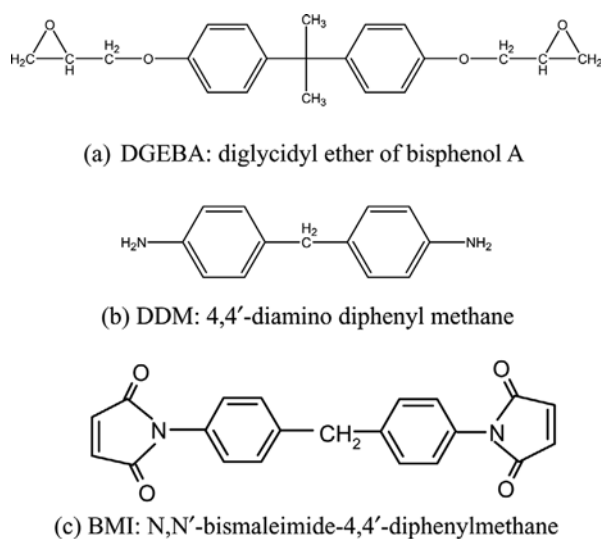(c) BMI: N,N′-bismaleimide-4,4′-diphenylmethane

Figure 1. Chemical structure of materials.

reported in Table I. For all the compositions, 30 phr of DDM is added into the DGEBA resin. The preparation of composite films was as follows. First, DGEBA and DDM were dissolved in NMP at 80 °C, vigorously stirred to obtain a homogeneous solution. Then, the appropriate amount of BMI was added. Mixing was continued at 80 °C to complete dissolution of the BMI powder. The reactive mixture so obtained was spin-coated onto 3 in silicon (100) substrate by using a spin-coater and cured at 160 °C for 2 h. Post curing was accomplished at 240 °C for 4 h. The ramping and cooling rates were 2.5 and 2.0 °C/min, respectively.

Measurements. Water sorption and diffusion behaviors were gravimetrically measured over temperature ranges of 5 ~60 °C using a Thin Film Diffusion Analyzer.[14,15] Furthermore, the water sorption behaviors were measured over relative humidities of 22~100% at 25 °C. The details are described in our previous studies.[14-17]

Dynamic mechanical thermal properties were conducted in a nitrogen ambient over the range of 25 ~ 300 °C, using a dynamic mechanical thermal analyzer (DMTA) (Polymer Laboratories Co., Model Mark III). The employed heating rate and frequency were 5.0 K/min and 1 Hz, respectively.

Decomposition temperature of the composite films was measured in a nitrogen ambient over the range of 25~ 800 °C, using a thermogravimetric analyzer (TGA) (TA Instruments Co.). Morphological studies were performed by a wide-angle x-ray diffraction (WAXD). WAXD patterns were collected by a wide-angle goniometer (Rigaku Co., Model RINT-2500H) with a monochromater. The Cu$K\alpha$ radiation source (λ=1.54 Å) was operated at 40 kV and 60 mA.

Results and Discussion

Thermal Properties. In the presence of aromatic amines, BMIs undergo two type of reactions as shown in Figure 2; (1) Michael addition reaction between the amino group and the double bond of BMI and (2) homopolymerization among themselves.[12] The amine reacts simultaneously with DGEBA and BMI, an intercrosslinked network will be formed. Whereas the reactivity of one of the two monomers is higher, a sequential interpenetrating polymer networks is likely to result. Therefore, the epoxy/BMI composites in the presence of aromatic amine DDM may belong to the intermediate situations in which the intercrosslinked network and interpenetrating polymer network may coexist, depending on the reaction conditions and on the composition of the reactive mixture.

The dynamic mechanical spectra for the epoxy/BMI composite films are depicted in Figure 3. The single and sym-
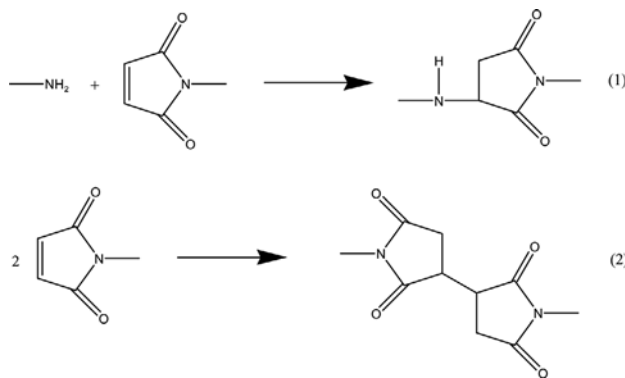

Figure 2. Reaction scheme of BMI in the presence of aromatic amine DDM.

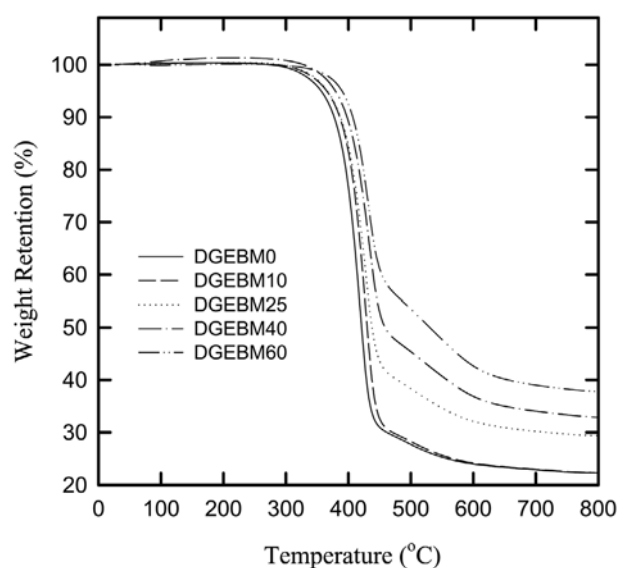**Table I. Compositions of the Investigated Epoxy/BMI Composites**

Composite Systems	Composition			DGEBA (wt %)	DDM (wt %)	BMI (wt %)
	DGEBA (parts/body wt)	DDM (parts/body wt)	BMI (parts/body wt)			
DGEBM0	100	30	-	76.82	23.08	-
DGEBM10	90	27	10	70.87	21.26	7.87
DGEBM25	75	22.5	25	61.22	18.37	20.41
DGEBM40	60	18	40	50.85	15.25	33.90
DGEBM60	40	12	60	35.71	10.72	53.57
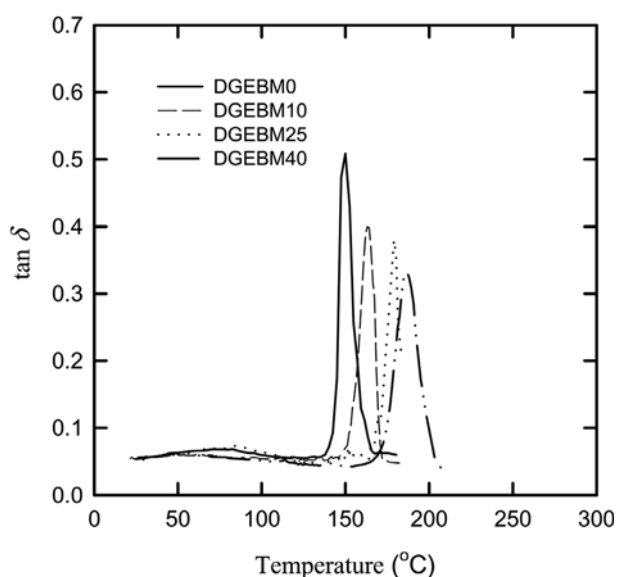
Figure 3. Tanδ as a function of temperature for the epoxy/BMI composite films.

Figure 4. TGA thermograms of the epoxy/BMI composite films.

metric damping peak-analogous to that observed in the neat DGEBA/DDM resin is detected for all the investigated composite films. In addition, its position shifts at higher temperatures as the BMI content increases. These results indicate that the formation of a single and homogeneous system, at least up to the scale of the dynamic-mechanical test; *i.e.*, the phase domain, if it exists, is smaller than the size of the segments that are responsible for the primary molecular relaxation.[18,19] The glass transition temperature of epoxy resin increased with BMI content as summarized in Table II.

Figure 4 shows TGA thermograms of the epoxy/BMI composite films. The 5 and 10 wt% loss temperatures were increased from 356 to 390 °C and 370 to 407 °C, respectively. Also, as the BMI content of the composite films increases, the percentage weight in residues increases. From the TGA results, it can be concluded that the crosslinked structure can increase the thermal stability of epoxy resin.[20] It may induce to the relatively high chain rigidity in BMI moiety and increase in the degree of crosslinking, which may result

in the enhanced thermal stability of the epoxy/BMI composite systems.

Water Sorption Behaviors. The water sorption behaviors for several EPOXY/BMI composite films (*i.e.,* DGEBM0, DGEBM25, and DGEBM60) were gravimetrically measured over humidities of 22~100% at 25 °C using aqueous solutions.[15,16] The obtained water sorption isotherms are depicted in Figure 5. The water sorption isotherms display a pronounced linear region extending up to about 60% of the total sorption range and are concave to the abscissa above the linear portion. This means that they were apparently well fitted to a Fickian diffusion model, despite the morphological heterogeneities due to the ordered and disordered phases.[13] It shows that the water sorption and diffusion behaviors in the neat epoxy and the composite films containing BMI should be patterned after a Fickian diffusion model, well below the glass transition temperature of the host. Thus, the diffusion coefficient and water uptake were calculated with the following equation, which was driven for an infinite slab with a constant surface concentration by

Table II. Properties of the Epoxy/BMI Composite Films

	Glass Transition Temperature (°C)	Weight Loss Temperature (°C)		Mean Intermolecular Distance[b]
		$T_{5wt\%}$	$T_{10wt\%}$	
DGEBM0	150	356	377	5.66 Å (15.8 °)
DGEBM10	163	365	386	5.60 Å (16.0 °)
DGEBM25	179	366	387	5.60 Å (16.0 °)
DGEBM40	187	379	398	5.50 Å (16.3 °)
DGEBM60	-[a]	390	407	5.43 Å (16.5 °)

[a]Not measured. [b]Calculated from the peak maximum of amorphous halo in the WAXD patterns.
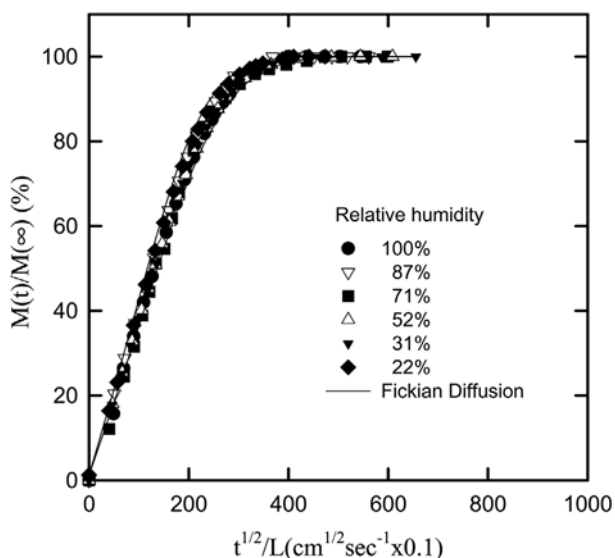
Figure 5. Water sorption isotherms of the DGEBM0 composite film measured over relative humidities of 22~100% at 25 °C.

Crank and Park.[13]

$$\frac{M(t)}{M(\infty)} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left(\frac{-D(2m+1)^2\pi^2 t}{L^2}\right) \qquad (1)$$

where $M(t)$ is the water sorption at a time t, $M(\infty)$ the water sorption at $t=\infty$, D the mutual diffusion coefficient of water and polymer system, and L the film thickness, respectively. Diffusion coefficients were estimated by best-fitting the measured diffusion isotherms with eq. (1). The results for the diffusion coefficient and water uptake are summarized in Figure 6.

The diffusion coefficient for the DGEBM0 composite film varied slightly in the range of 1.8×10^{-8} to 2.3×10^{-8} cm²/sec over relative humidities of 22~100%. Apparently, the water diffusion coefficient was nearly invariant with various humidities within experimental error as shown in Figure 6. It indicates that the water diffusion in the DGEBM0 composite film apparently obeys Fick's second law, which assumes that the diffusion coefficient is constant and not a function of concentration in films. Furthermore, this result suggests that the DGEBM0 composite film is relatively homogeneous, and water molecules are uniformly distributed in a more or less uniform manner. The other two composite films showed similar results with the DGEBM0 composite film. The diffusion coefficient varied slightly with humidity in the range of 1.7×10^{-8} to 2.0×10^{-8} cm²/sec for the DGEBM25 composite film and 1.4×10^{-8} to 1.6×10^{-8} cm²/sec for the DGEBM60 composite film, respectively. The apparent diffusion coefficient in the composite films as a function of relative humidity is approximately constant, which indicates that the water seems to be in a relatively constant environment regardless
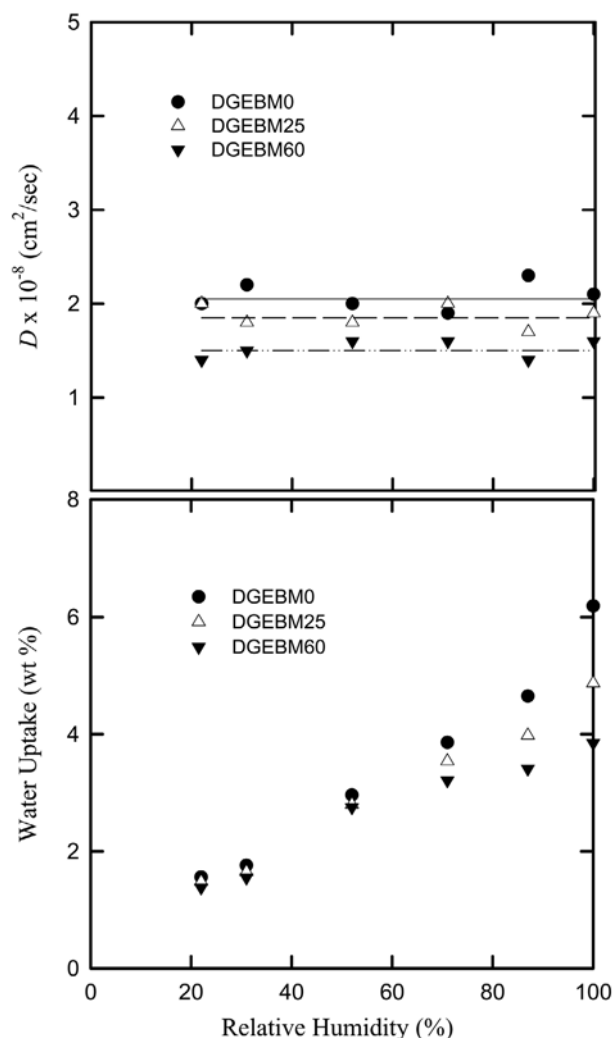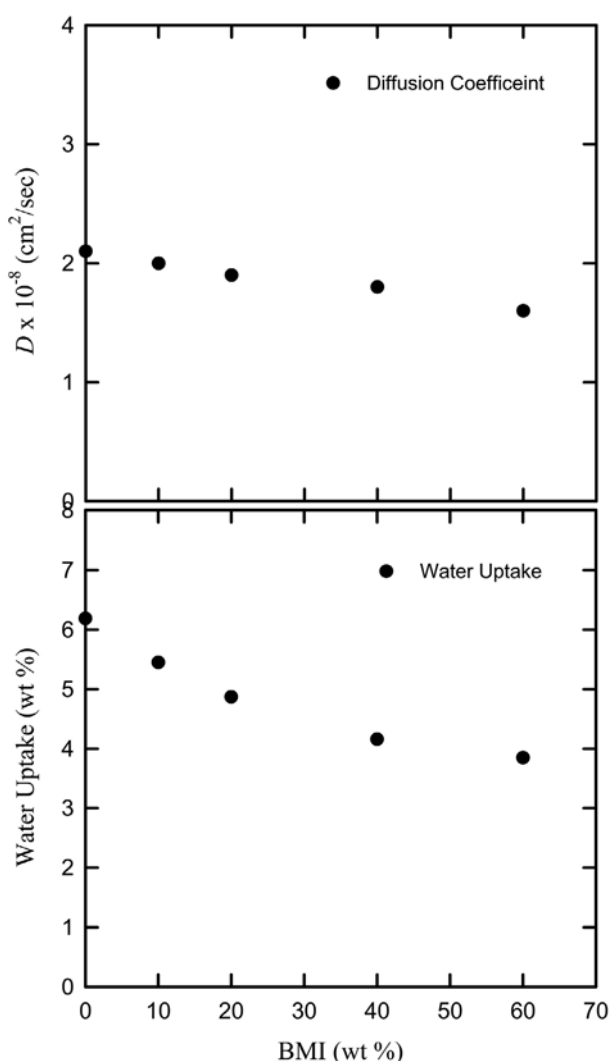

Figure 6. Effect of humidity on the diffusion coefficient and water uptake of epoxy/BMI composite films measured over relative humidities of 22~100% at 25 °C.

of the degree of water vapor concentration. These are consistent with our previous results for the polyimide films[15-17] and several researchers' results.[21,22] However, the average value in the diffusion coefficient decreased with increasing BMI content: DGEBM0 (2.05×10^{-8} cm²/sec) > DGEBM25 (1.85×10^{-8} cm²/sec) > DGEBM60 (1.50×10^{-8} cm²/sec).

In contrast to the diffusion coefficient, the water uptake was clearly a function of humidity as shown in Figure 6. For the DGEBM0 composite films, the water uptake increased with increasing relative humidity from 1.56 wt% in 22% relative humidity to 6.19 wt% in 100% relative humidity. For the other composite films, the water uptake is nearly a linear function of relative humidity as with DGEBM0 composite film. It means that water sorption mechanisms of the composite films in this study obey Henry's law.[13]

In Figure 7, the effects of BMI on the diffusion coefficient and equilibrium water uptake are represented as a function

Figure 7. Effect of BMI on the diffusion coefficient and water uptake of the epoxy/BMI composite films measured at 25 °C and 100 % relative humidity.

of the weight ratio of BMI. The water sorption behaviors were strongly dependent upon the compositions of the composite films, which may come from the variations of chemical structure and morphological structure by incorporating BMI. The water diffusion coefficient varied in the range of 2.1×10^{-8} ~1.6×10^{-8} cm²/cm and water uptake did in the range of 6.19 ~3.85 wt%, respectively. It is noted that both equilibrium water uptake and water diffusion rate apparently decreased with increasing the BMI content. The dependence of the content of BMI on the water sorption behaviors may be attributed to some changes in the chemical structure and morphological structure in the composite films with incorporating BMI.

The water diffusion in the epoxy/BMI composite films was further investigated over the temperature ranges of 5~60°C and depicted in Figure 8. With increasing temperature, the diffusion coefficient increased from 1.0×10^{-8} to 5.5×10^{-8}
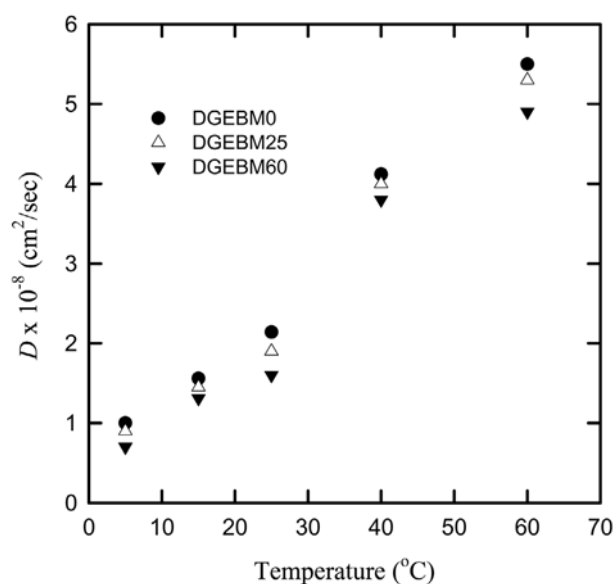

Figure 8. Effect of temperature on the diffusion coefficient of the epoxy/BMI composite films.

cm²/sec for the DGEBM0 composite film, 0.9×10^{-8} to 5.3×10^{-8} cm²/sec for the DGEBM25 composite film, and 0.7×10^{-8} to 4.9×10^{-8} cm²/sec for the DGEBM60 composite film, respectively. These increases in the diffusion coefficient with increasing temperature may be due to the increase in the mobility or flexibility of the polymer chains at an elevated temperature which enlarges the free volume among the polymer chains. It makes water molecules more penetrable through polymer chains, which results in the increase of diffusion coefficient.

The activation energy is needed for water diffusion processes since the water molecules have to overcome the energy barriers set up by the interaction potential from intramolecular forces.[20,23] The activation energy for the water diffusion was calculated from the diffusion coefficients on the basis of the Arrhenius relationship as follows:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \qquad (2)$$

where D (cm²/sec) is the diffusion coefficient at a temperature T (K), D_0 (cm²/sec) the pre-exponential factor, E_a (kcal/mol) the activation energy for the water diffusion, and R the gas constant (1.98 kcal/mol K), respectively. As shown in Figure 9, the plots of ln$D$ vs $1/T$ exhibit a fairly linear relationship. The activation energy was simulated from the best-fitting to eq. (2). With increasing content of BMI, the activation energy increased for the composite films: DGEBM0 (5.87 kcal/mol) < DGEBM25 (6.12kcal/mol) < DGEBM60 (6.61 kcal/mol). It indicates that the ability of water molecules to diffuse through polymer chains is reduced by with increasing BMI content. The higher value of the activation
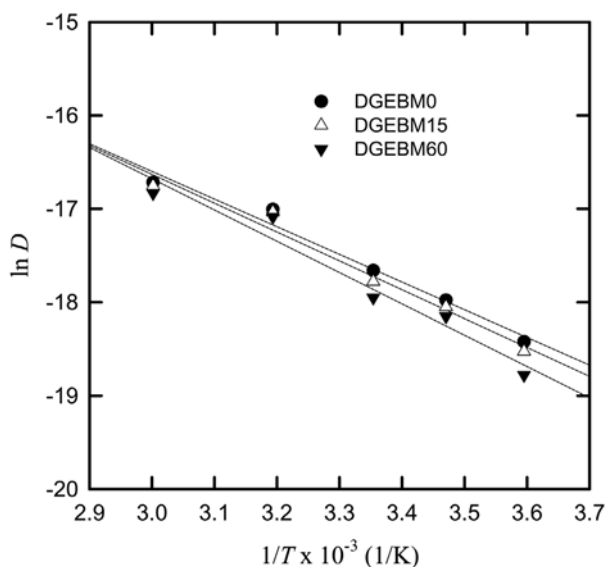
Figure 9. Relationships between ln$D$ and $1/T$ for the epoxy/BMI composite films.

energy in the DGEBM60, which indicates the enhanced hydrolytic stability in the DGEBM60 composite films, is related to the different network structure (morphological structure) caused by incorporating BMI.

Generally, it has been known that the water sorption and diffusion behaviors in polymer films can be interpreted by considering two major contributory factors, chemical structure and morphological structure. In the aspect of chemical structure in polymer films, a high concentration of polar functional groups can promote increased sorption of polar penetrants. Epoxies generally form three-dimensional networks of covalent bonds derived from initially monomeric component.[5,9,10] To create these covalent networks, reactive polar groups are utilized in the initial monomers. Typically, primary or secondary amines are used as the reactive species in the curing agent to open the glycidal rings of an epoxide, thus creating a hydroxyl group. This incorporates both the hydroxyl and the amine in to the covalent network. The epoxide groups of DGEBA react with the hydrogens of -NH$_2$ and -NH- groups according to the following reaction: This reaction leads to the formation of hydroxyl (-OH) groups, which show strong hydrophilic character. In general, the more polar groups present in the polymer matrix, the higher will be its sorptive affinity toward water.

From the trend of the water sorption data, there appears to be a strong link between the BMI content of the composites and the water sorption that it plays. These composite films containing large amounts of BMI display low values of diffusion coefficient and water uptake than those containing low amounts of BMI. By increasing the weight ratio of incorporating BMI, the relative content of hydroxyl groups in epoxy matrix decreases as shown in Table I. It may induce to rela-

tively small amount of water uptake and slow diffusion in the composite films containing relatively high content of BMI.

In addition to the chemical structure, the morphological structure must be considered in a discussion on the water sorption in the composite films. Morphological structure refers to the spatial configuration of the molecular segments in the network. Different configurations can result in a more "open" structure, which should influence how much moisture is sorbed. For example, the molecules of a polymer crystal pack together very efficiently, and leave very little room for a penetrant molecule. Consequently, crystalline polymers absorb very little water. In polymer glasses, such as epoxy, the packing is far less efficient, and there is ample room for a small penetrant molecule, such as water, to occupy.

Some information about the morphological structure in the composite films was investigated using the WAXD measurement. The measured WAXD patterns are depicted in Figure 10. All the composite films exhibited only one amorphous and broad halo peak in the diffraction patterns over the range of 10 to 35°, despite the variation in compositions by incorporating BMI. It indicates that the neat epoxy resin film and four different composite films containing crosslinkable BMI are nearly amorphous and structureless, and have poor ordering in polymer chains.

However, the height of amorphous halos for the composite films was increased with increasing content of BMI. Specifically, the DGEBM40 and DGEBM60 composite films exhibited the slight indication at about $2\theta = 10°$, which is the representative diffraction for the intramolecular packing order. These WAXD patterns indicate that the order in polymer chains and intramolecular packing order slightly increased by incorporating BMI. In addition to the characteristic dif-
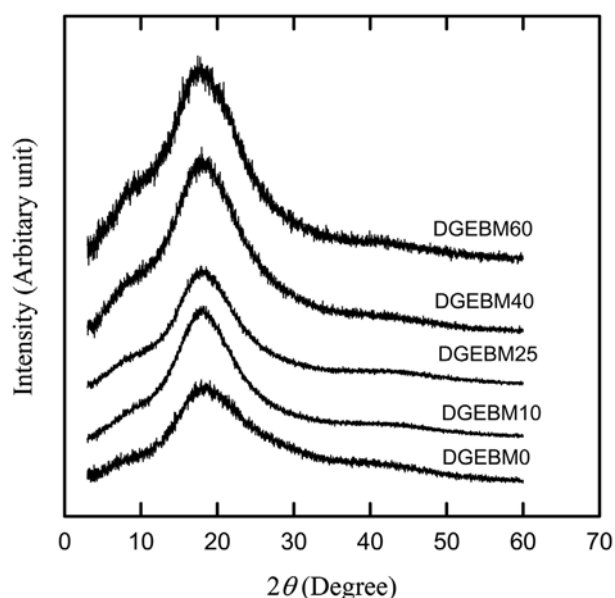
Figure 10. WAXD patterns of the epoxy/BMI composite films.

fraction peaks, the mean intermolecular distances were calculated from the peak maximum of the reflection WAXD patterns and summarized in Table II. The mean intermolecular distances are critical factors for the water sorption and diffusion behaviors in polymer films.[14,24] The mean intermolecular distance decreased with increasing content of BMI, which indicates that the lateral packing order of polymer chains is enhanced for higher content of BMI. It may be attributed to BMI incorporation and increase in the degree of crosslinking in the composite films.

As described above, the incorporation of BMI in epoxy resin will change both the chemical structure and morphological structure in epoxy/BMI composite films.[25,26] As the BMI content in the composite films increases, it will decrease the relative content of hydroxyl groups in epoxy matrix and increase the intermolecular packing order in polymer chains, which may serve to the resistance to water sorption and diffusion in the epoxy/BMI composite films.

Conclusions

Epoxy/BMI composite films were prepared using *N,N'*-bismaleimide-4,4'-diphenylmethane (BMI) as a crosslinkable moiety, diglycidyl ether of bisphenol-A (DGEBA) as a epoxy resin, and 4,4'-diamino diphenyl methane as a amine hardner. The water sorption behaviors in epoxy/BMI composite films were gravimetrically investigated as a function of humidity, temperature, and composition of epoxy/BMI composites. The glass transition temperature and thermal stability of epoxy resin were increased with increasing content of crosslinkable imide moiety BMI. As the content of BMI in epoxy/BMI composite films increases, the diffusion coefficient and water uptake decreased and the activation energy for water diffusion increased. The water sorption behaviors in BMI in epoxy/BMI composite films were closely related to the chemical structure and morphological structure. By increasing the weight ratio of incorporating BMI, the relative content of hydroxyl groups in epoxy matrix decreases and the intermolecular packing order in the epoxy/BMI composite films is enhanced, which may induce the increased resistance to water sorption and diffusion in the epoxy/BMI composite films containing relatively high content of BMI.

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