

# Water Sorption and Diffusion Behaviors in Composite Films of Poly(ether imide) and Bismaleimide

Jongchul Seo, Choonkeun Lee, Wonbong Jang, Saimani Sundar, Haksoo Han

Department of Chemical Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemun-Gu, Seoul, 120-749 Korea

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**ABSTRACT:** The effect of a crosslinkable imide moiety, bismaleimide (BMI), on the water sorption properties of poly(ether imide) (PEI) was gravimetrically measured and interpreted together with the chemical and morphological structures in composite films. The morphological structure of composite films was investigated by using a prism coupler and X-ray diffraction pattern. It indicated that the in-plane orientation and intermolecular packing order increased as the content of BMI in composite films increased. The water sorption behaviors showed dependence on the

morphological change originating from the addition of BMI to PEI. The composite film with relatively high content of BMI exhibited a relatively high degree of in-plane orientation and a small mean intermolecular distance, which resulted in a decrease in the diffusion rate and water sorption and an increase in the activation energy in composite films. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1692–1697, 2006

**Key words:** polyimide; bismaleimide; interpenetrating network; water sorption; morphology

## INTRODUCTION

Aromatic polyimides possess outstanding thermal, mechanical, and electrical properties, as well as excellent chemical resistance. Ultem 1000, a poly(ether imide) (PEI), has received significant attention from both academia and industry. It is an amorphous polymer offering high strength, excellent flame and heat resistance, and good melt processability. There is no appreciable loss in mechanical properties up to 170°C, making it ideal for high strength and high heat applications and those requiring consistent dielectric properties over a wide frequency range. PEI is commonly used in electrical and electronic insulators (including many semiconductor process components) and a variety of structural components requiring high strength and rigidity at elevated temperatures.<sup>1–3</sup>

However, the monomeric unit of PEI contains two ether groups, four carbonyl groups, and two imide groups that are hydrophilic (see Fig. 1). In addition, these groups may hinder the order of interaction in the polymer and lead to the amorphous and structureless morphology in PEI.<sup>4</sup> The high concentration of polar groups and poor morphological structure of PEI lead to relatively high water sorption. The water sorption causes potential reliability problems in microelectronic devices,<sup>5–10</sup> such as displacement, package

crack, delamination, loss of adhesion, potential corrosion, and mechanical failures in thin films.

To reduce the water sorption in PEI, semi-interpenetrating polymer network (semi-IPN) composite films were prepared from PEI and crosslinkable imide moiety bismaleimide (BMI). The water sorption behaviors of the composite films were gravimetrically investigated by using a thin film diffusion analyzer,<sup>11–15</sup> and they were correlated with the chemical and morphological structures of composite films. The morphological structures in films were characterized by wide-angle X-ray diffraction (WAXD) and prism coupling techniques.

## EXPERIMENTAL

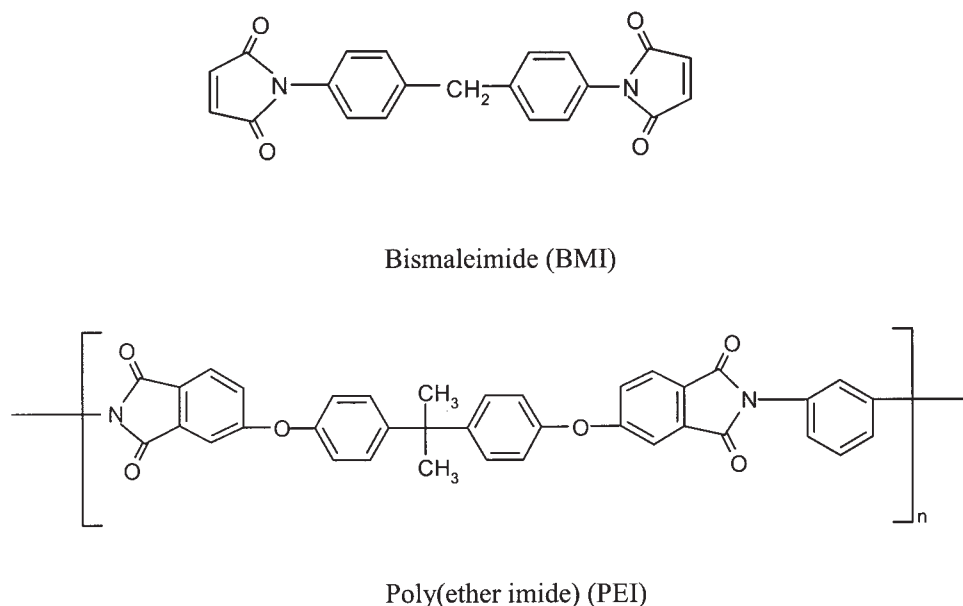
### Materials

The chemical structures of BMI and PEI are shown in Figure 1. BMI powder was purchased from Aldrich Chemical Co. General Electric supplied PEI (Ultem 1000), which is an amorphous thermoplastic with a number-average molar mass of 20 kg mol<sup>-1</sup>, a density of 1.27, and a glass-transition temperature of ~250°C. PEI was dried under a vacuum for 24 h at 80°C to remove moisture prior to use.

Various composite films were prepared by dissolving BMI and PEI in *N*-methyl-2-pyrrolidone. The solid content of the polymer composite solution was 15 wt %. Composite films were prepared by spin coating of a mixed solution, followed by thermal treatment at 300°C. The ramping and cooling rates were 2.5 and 2.0°C/min, respectively. The thickness of the

Correspondence to: H. Han (shan@yonsei.ac.kr).

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**Figure 1** The structures of bismaleimide and poly(ether imide).

composite films was controlled in the 10–13  $\mu\text{m}$  range by a spin coater<sup>11–14</sup> and measured using a surface profiler (model AS500, Tencor Instruments Co.). Then, the cured films were detached from the substrates with the aid of deionized water, washed with distilled water several times, and dried under a vacuum for 24 h.

The composite films thus obtained are designated on the basis of constituents and blend composition. For example, the composite films of PEI containing 0, 10, 25, 40, and 60% (w/w) BMI are represented by UTBM0, UTBM10, UTBM25, UTBM40, and UTBM60, respectively. The letters UT and BM stand for PEI and BMI, respectively, and the numerals represent the weight percent of BMI.

### Measurements

The water sorption behaviors of the composite films were gravimetrically investigated by using a thin film diffusion analyzer (model D-200, CAHN Instruments Co.). Measurements were carried out in a temperature range of 5–60°C. The details are described in our previous studies.<sup>11–15</sup>

The refractive indices of the composite films were measured by a prism coupler (model 2010, Metricon Inc.) with 632.8-nm wavelength He-Ne laser light. In the measurements the resolution of the refractive index was  $\pm 0.0005$ . A combination of transverse electric (TE) mode and transverse magnetic (TM) mode was used for measuring the in-plane and out of plane refractive indices. WAXD patterns were obtained with a wide-angle goniometer (model RINT 2500H, Rigaku

Co.) with a monochromator (flat crystal type). The Cu K $\alpha$  radiation source ( $\lambda = 1.54 \text{ \AA}$ ) was operated at 40 kV and 60 mA, and all measurements were carried out in  $\theta/2\theta$  mode. Diffractograms were collected over 5–60° ( $2\theta$ ) at 0.02° intervals with a scan speed of 0.3–0.5°  $\text{min}^{-1}$ .

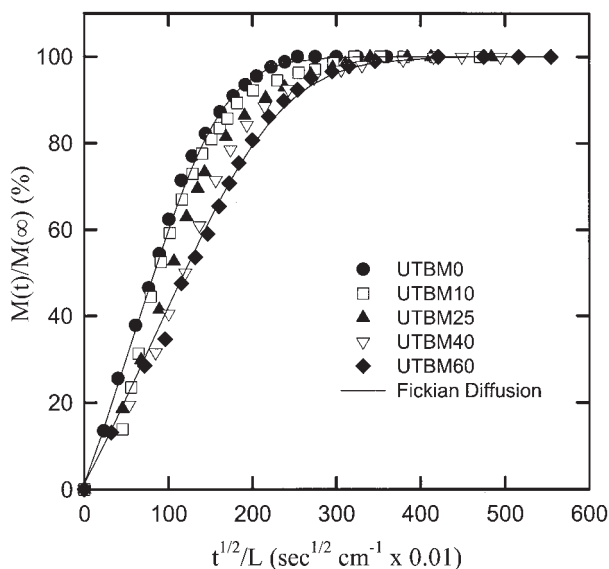
## RESULTS AND DISCUSSION

### Water sorption

Figure 2 shows the water sorption curves measured at 25°C and 100% relative humidity. The water sorption curves displayed a pronounced linear region extending up to about 60% of the total sorption range. This means that they were apparently well fit to a Fickian diffusion model, despite the morphological heterogeneities due to the ordered and disordered phases.<sup>16</sup> It shows that the sorption behavior of small molecules in polymers 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 used for an infinite slab with a constant surface concentration by Crank<sup>17</sup>:

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

where  $M(t)$  is the water sorption at a time  $t$ ,  $M(\infty)$  is the water sorption at  $t = \infty$ ,  $D$  is the mutual diffusion



**Figure 2** The water sorption isotherms of the composite films measured at 25°C and 100% relative humidity.

coefficient of the water and polymer system, and  $L$  is the film thickness. The results for the diffusion coefficient and water uptake are summarized in Figure 3.

With increasing content of BMI, the diffusion coefficient and water uptake varied in the range of  $(12.8\text{--}10.5) \times 10^{-10} \text{ cm}^2/\text{s}$  and 4.60–2.95 wt %, respectively. Apparently, the diffusion coefficient and water uptake decreased with increasing content of crosslinkable imide moiety BMI, as shown in Figure 2. This indicates that the hydrolytic stability of PEI was higher in the composite systems.

The water diffusion processes in polymer films are basically energy-activated processes obeying the Arrhenius relationship. The activation energy for water diffusion is needed to enable water molecules to diffuse through polymer chains. It is strongly dependent on the nature of the diffusant; the nature of the polymer; and modifications of the polymer, such as crosslinking, plasticizing, crystallizing, and fillers. In the present study, thermoplastic PEI was modified by incorporating a crosslinkable imide moiety BMI, consequently leading to variations in the crosslinking, crystallinity, molecular order in polymer chains, and so forth. Note from Figure 3 that both the water uptake and diffusion coefficient decreased with an increase in BMI content because of the increase in crosslinking.

To investigate the effect of temperature on the water diffusion behavior, water sorption curves were measured for three composite films: UTBMO, UTBM25, and UTBM60. The measurements were conducted in a temperature range from 5 to 60°C, and the results are depicted in Figure 4.

All the sorption curves were reasonably well fitted to a Fickian diffusion model, regardless of tempera-

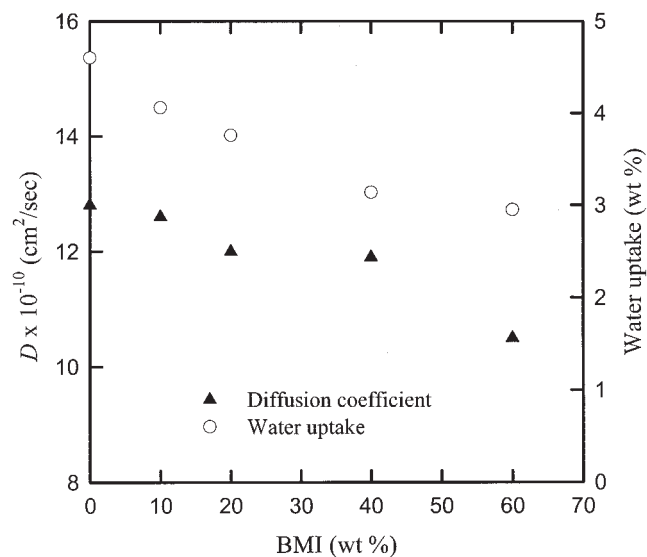
ture and morphological heterogeneities. Thus, the diffusion coefficients were calculated using eq. (1) and are provided in Table I.

The diffusion coefficient for UTBMO varied from  $(5.1 \text{ to } 26.0) \times 10^{-10} \text{ cm}^2/\text{s}$  and apparently increased with increasing temperature. Similar results were also observed for UTBM25 and UTBM60 composite films. The increase in the diffusion coefficient with increasing temperature may be attributable to the increase in the mobility or flexibility of the polymer chains at elevated temperature, which enlarges the free volume among the imide chains. Hence, the penetration of water molecules through polymer chains increased, which resulted in the increase of the diffusion coefficient. However, the effect of temperature on the diffusion behavior of the semi-IPN composite films also increased with an increase in temperature, and the diffusion coefficient values decreased with an increase in the crosslinkable imide moiety BMI.

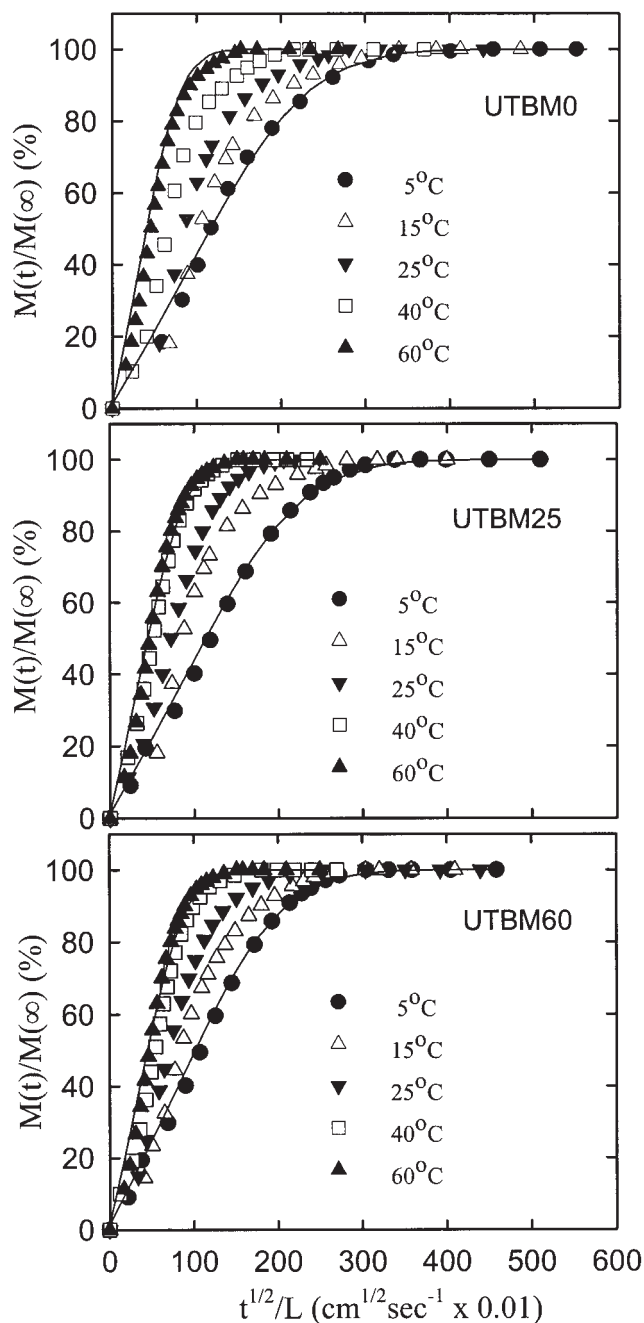
The activation energy for the water diffusion was calculated from the diffusion coefficients on the basis of the Arrhenius equation as follows:

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

where  $D$  ( $\text{cm}^2/\text{s}$ ) is the diffusion coefficient at a temperature  $T$  (K),  $D_0$  ( $\text{cm}^2/\text{s}$ ) is the preexponential factor,  $E_a$  (kcal/mol) is the activation energy for the water diffusion, and  $R$  is the gas constant (1.98 kcal/mol K). As depicted in Table II, the plots of  $\ln D$  versus  $1/T$  exhibit a fairly linear relationship. It implies that the diffusion kinetics of water molecules for the composite films does not change with varying temperatures.<sup>17</sup>



**Figure 3** The diffusion coefficient and water uptake in the composite films.



**Figure 4** Water sorption isotherms of the composite films measured in the temperature range of 5–60°C.

The activation energies for the UTBM composite films were calculated from the best fit to eq. (2).

The activation energies showed dependence on the content of crosslinkable imide moiety BMI. With increasing BMI content, the activation energy for the composite films apparently increased with increasing content of BMI: 5.69 kcal/mol for UTBM0, 5.71 kcal/mol for UTBM25, and 5.89 kcal/mol for UTBM60. In addition, the  $D_0$  increased with increasing content of BMI: UTBM0 ( $0.16 \times 10^{-4}$ ) < UTBM25 ( $0.17 \times 10^{-4}$ ) < UTBM60 ( $0.21 \times 10^{-4}$ ). This is similar to other

previous results.<sup>18,19</sup> These variations in activation energy and  $D_0$  indicate that the ability of water molecules to diffuse through polymer chains is reduced with increasing BMI content. These results showed good agreement with those of the diffusion coefficient, as shown in Figure 3. The difference in the activation energy with compositions may be attributed to the difference in the chemical and/or morphological structure, such as the crystallinity, chain orientation, and packing order.<sup>5,11,12</sup>

### Morphological structure

The water sorption behaviors of polymer films are usually correlated to the chemical structure and/or morphological structure. PEI contains two hydrophilic ether linkages per one repeating unit in the polymer backbone.

The in-plane ( $n_{xy}$ ) and out of plane ( $n_z$ ) refractive indices of the composite films were measured with the prism coupler at 632.8 nm, and the results are summarized in Table III.

All the composite films showed larger  $n_{xy}$  than  $n_z$ , regardless of the compositions of the composite films. This indicates that polymer chains are preferentially aligned in the film plane, resulting in positive birefringence ( $\Delta$ ) in the composite films. However, with an increase in the BMI content, the  $n_{xy}$  increased, consequently leading to increases in both the average refractive index [ $n_{av} = (2n_{xy} + n_z)/3$ ] and film birefringence. It indicates that the molecular in-plane orientation is enhanced as the content of BMI increases. These variations in refractive indices are attributed to the polarizabilities of carbon atoms consisting of BMI monomer and a decrease in the free volume of the composite films. In general, higher polarizability causes a higher dipole moment under an electromagnetic field, providing a higher refractive index.

Furthermore, the morphological structures in the UTBM composite films were investigated using the WAXD measurement. The WAXD patterns for the UTBM composite films are depicted in Figure 5. Despite the variation in compositions by incorporating BMI, all composite films showed only one amorphous halo, which indicates that the composite films are nearly amorphous and structureless. This may be due

**TABLE I**  
Diffusion Coefficients of Composite Films Measured from 5–60°C

Composite systems	Diffusion coefficient ( $\text{cm}^2/\text{s}$ )				
	5°C	15°C	25°C	40°C	60°C
UTBM 0	5.1	7.8	12.8	22.3	26.0
UTBM 25	5.1	7.4	12.0	22.0	25.3
UTBM 60	4.7	7.6	10.5	20.7	25.5

TABLE II  
Relationships Between  $\ln D$  and  $1/T$  for Composite Films

Composite systems	$1/T \times 10^{-3}$ (1/K)				
	3.5952	3.4704	3.3540	3.1934	3.0016
UTBM 0	-21.3966	-20.9717	-20.4764	-19.9213	-19.7678
UTBM 25	-21.3966	-21.0244	-20.5409	-19.9348	-19.7950
UTBM 60	-21.4783	-20.9977	-20.6745	-19.9957	-19.7872

to the flexible and bulky internal linkages of PEI, which are two ether ( $-\text{O}-$ ) and two methyl ( $-\text{CH}_3$ ) groups.

However, the height of the amorphous halos increased with increasing content of BMI. Specifically, the UTBM semi-IPN composite films exhibited a slight indication at about  $2\theta$   $10^\circ$ , which increased with increasing content of BMI. These WAXD patterns indicated that the molecular order in polymer chains and intramolecular packing order was increased by incorporating the crosslinkable monomer BMI. These WAXD results showed good agreement with the prism coupler results. In addition to the characteristic diffraction peaks, the mean intermolecular distances were calculated from the peak maximum of the amorphous halo in the reflection WAXD patterns and are summarized in Table III. The mean intermolecular distances are critical factors for water sorption and diffusion in polymer films.<sup>11,12,20</sup> As shown in Table III, 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 crosslinking monomer BMI. It may be attributed to the increase in the crosslinking of the semi-IPN composite films with an increase in the BMI content.

As mentioned, the morphological structures in the UTBM composite films were strongly dependent upon the compositions. All of the semi-IPN composite films exhibited structureless and amorphous structures. However, the in-plane orientation and intermolecular packing order increased with increasing BMI content,

which indicated an increase in crosslinking. It is well known that highly packed and crystalline phases serve as impenetrable obstacles that diminish the volume available for water sorption,<sup>14,15</sup> because the distances between polymer chains are too small to allow water molecules to pass through them. This means that a high degree of in-plane orientation, high crystallinity, and small mean intermolecular distance will make it more difficult for water molecules to diffuse in the out of plane direction, which results in a low diffusion coefficient and high activation energy in the polymers with well-ordered structure. These morphological differences with the increase of BMI content in the UTBM composite films might reflect directly on the activation energy and water sorption/diffusion behaviors.

## CONCLUSIONS

The effect of the addition of a crosslinkable imide moiety BMI on the water sorption properties into PEI was gravimetrically measured and interpreted in accordance with the chemical and morphological structures in composite films. With increasing content of BMI, the diffusion coefficient and water uptake varied in the range of  $(12.8-10.5) \times 10^{-10}$   $\text{cm}^2/\text{s}$  and 4.60–2.95 wt %, respectively. The activation energy for the composite films apparently increased with an increase in the BMI content at 5.69 kcal/mol for UTBM0, 5.71 kcal/mol for UTBM25, and 5.89 kcal/mol for UTBM60. The morphological structure of composite films, which was investigated using a prism coupler

TABLE III  
Optical Properties and Mean Intermolecular Distances of Composite Films

Composite systems	Film thickness ( $\mu\text{m}$ )	Mean intermolecular distance <sup>a</sup> (Å)	Optical properties at 632.8 nm			
			$n_{xy}$	$n_z$	$n_{av}$ <sup>b</sup>	$\Delta$ <sup>c</sup>
UTBM0	12.52	5.37	1.6539	1.6498	1.6525	0.0041
UTBM 10	11.11	5.16	1.6607	1.6563	1.6592	0.0044
UTBM 25	11.42	5.13	1.6629	1.6569	1.6609	0.0060
UTBM 40	10.98	5.08	1.6675	1.6562	1.6637	0.0113
UTBM 60	11.68	4.99	1.6676	1.6567	1.6640	0.0109

<sup>a</sup> Calculated from the peak maximum of the amorphous halos in the WAXD patterns.

<sup>b</sup>  $n_{av} = (2n_{xy} + n_z)/3$ .

<sup>c</sup>  $\Delta = n_{xy} - n_z$ .

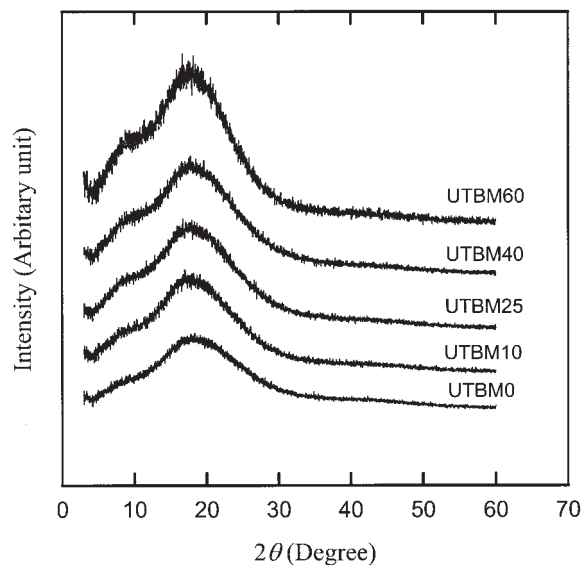


Figure 5 WAXD patterns of the composite films.

and X-ray diffraction pattern, indicated that the in-plane orientation and intermolecular packing order increased as the content of BMI in composite films increased. The composite film with relatively high content of BMI exhibited a relatively high degree of in-plane orientation and small mean intermolecular distance, which resulted in a lower diffusion rate, lower water sorption, and high activation energy.

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