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Morphology effect on water sorption behavior in a thermoplastic modified epoxy resin system

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Abstract

Water sorption behavior in polyetherimide (PEI) modified diglycidyl ether bisphenol-A/4,4′-diaminodiphenyl sulfone (DGEBA/DDS) systems was investigated by gravimetric analysis, positron annihilation lifetime spectroscopy and scanning electron microscopy. The equilibrium water uptake showed strong composition-dependent, which suggested that hydrophilic groups rather than free volume were more significant in determining ultimate water sorption. While besides the number of hydrophilic groups and fractional free volume, morphology induced by phase separation was another key factor that decided the value of diffusion coefficient, which was chiefly responsible for the anomalous diffusion behavior observed at the beginning of co-continuous phase. In addition, morphology not only had the function of decreasing fractional free volume, but also changed the number of hydrophilic groups in epoxy rich regions, which obviously distinguished water sorption behavior in the blends from that in single component systems.

Keywords: Hydrophilic group; Fractional free volume; Water sorption behavior

1. Introduction

The behavior of water diffusion in epoxy or modified epoxy networks is a fascinating focus that scientists have been caring for a long time [1–6], for excellent properties of epoxy materials will be greatly affected by the water absorbed and thus its potential application is confined. Due to different experimental methods, several models with certain evidential phenomena argue the state of water molecules in epoxy networks. Woo and Piggott [7] suggested clustering of water molecules in epoxy resins. Adamson [8] concluded that water molecules first occupy free volume holes then become bound to specific chain segments or groups, while Moy [9] reported that existence of free/bound types of water molecules is due to different water vapor concentrations. Apicella et al. [10] proposed three sorption models in glassy epoxy: bulk dissolution of water in glassy epoxy networks; moisture sorption onto the surface of excess free volume; hydrogen bonding between water and polymer hydrophilic groups. In addition, Zhou [3] found recently two types of water in epoxy resins in which one disrupted the inter-chain interaction, the other formed multiple hydrogen-bonding with epoxy networks. However, no single theory existed is able to support all sorption phenomena and water diffusion modes with related mechanisms are still not fully understood.

In our previous works, water diffusion behavior in novolac epoxy networks has long been studied, and valuable information are available on contributions of not only the free volume and hydrophilic groups of networks, but also the polarity and flexibility of side groups [11–13].

The fragile nature of epoxy resins can be improved by introduction of a second component that is capable of phase separation such as rubbers and thermoplastic polymers. Generally, linear thermoplastic polymers are inherently tough and can reduce the brittleness of the resin without affecting their advantageous ultimate properties, which has been studying with great interest [14–18]. However, water sorption still remains a serious problem. Although efforts have been made to ascertain the water sorption behavior in thermoplastic modified thermosets by Pethrick using poly (ether sulfone)-amine-cured epoxy resins [18], few papers have been published on this subject.

In recent years, positron annihilation lifetime spectroscopy

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Table 1
Composition of blends

Blend code	DGEBA (weight)	PEI (weight)	DDS (weight)
EP	100	0	31
5-phr	100	5	31
10-phr	100	10	31
15-phr	100	15	31
20-phr	100	20	31
PEI	0	100	0

(PALS) has emerged as a new microanalytical probe, which is capable of directly probing the size and content of free volume in polymers [17,19,20]. In the experiments, the radioisotope ^{22}Na is commonly used as a positron source, from which average energies of 210 keV are emitted. These energetic positrons loose their energy in substances, through inelastic collisions, and finally annihilate with electrons, while emitting 0.511 MeV gamma rays. There are two spin states of positronium (Ps) known as *ortho*-Ps (*o*-Ps) and *para*-Ps (*p*-Ps) with lifetimes of 142 and 0.125 ns, respectively. In addition, *o*-Ps seeks intermolecular-space holes and can remain inside them until it picks up electrons from the walls of the holes. Then, the annihilation of the *o*-Ps component can be treated as a measure of free volume inside polymers, with lifetime and intensity strongly dependent on the size and distribution of free volume sites, respectively [21,22]. Based on this technique, the physical aging [23] and water absorption [24–27] of epoxy resin have also been discussed.

In the present work, we monitor the water sorption behavior in a series of different content polyetherimide (PEI) modified diglycidyl ether bisphenol-A/4,4′-diaminodiphenyl sulfone (DGEBA/DDS) systems by gravimetric measurements, PALS and scanning electron microscopy (SEM). The key factors on water sorption in the blends are discussed, and the effect of morphology on the subject that has long been neglected is put forward.

2. Experimental section

2.1. Materials

The polyetherimide (PEI, $[\eta] = 0.73$, $T_g = 218$ °C) was synthesized in one step from bisphenol-A dianhydride (BISA-DA) and 4,4-[1,3-phenylenebis (1-methylethylidene)] bisaniline (BISM-diamine) with stoichimetric ratio 1:0.98 (mole ratio) in *m*-cresol at 200 °C for 6 h [28]. The structure (Fig. 1) is depicted below:

The cure agent 4,4′-diaminodiphenyl sulfone (DDS) (Shanghai Third Reagent Factory) and the epoxy oligomer diglycidyl ether bisphenol-A (DGEBA) (DOW Chemical, Epon 828) were used without further purification.

2.2. Film preparation

The epoxy resin and hardener were used as supplied in weight ratio of 31 phr (parts per hundred resin), while samples were prepared with PEI fractions from 5 to 20 phr. The blends were produced by mixing the PEI and DGEBA at 145 °C until the mixture was homogeneous, followed by degassed under vacuum, and then DDS was added promptly at 105 °C. After thoroughly stirred under reduced pressure, the solution was swiftly poured onto a 76 mm × 15 mm × 4 mm aluminum mold, which was cured in the vacuum oven at 180 °C/3 h and postcured at 200 °C/2 h afterwards. The curing process of EP was same as above, while PEI was gained by molding.

The compositions of epoxy/PEI blends are listed in Table 1.

2.3. Gravimetric measurements

The sample sheets (10 mm × 10 mm × 1 mm) were polished with distilled water and then dried under vacuum oven at 85 °C for a week. Water sorption in the resins as the function of immersion time was monitored by gravimetric method. The samples were periodically removed from the water of 40 °C, wiped down and quickly weighed on a Tg332A microbalance (accuracy: 0.01 mg).

2.4. Positron annihilation lifetime spectroscopy

Positron annihilation experiments of specimens were conducted on a multichannel analyzer data buffer (Ortec Adcam mode) with a time resolution of 0.27 ns full-width at half-maximum (fwhm). The probe consists of BaF_2 crystal and XP2020Q PMT. About 20 μ of Ci Na^{22}Cl was directly deposited on one of the samples and then sandwiched between two identical pieces of the samples (12 mm × 12 mm × 1.4 mm). Each spectrum were collected over about 2 h period and consisted of about 10^6 integrated counts. The spectra were analyzed using the program PATFIT.

2.5. Scanning electron microscopy

The morphologies of impact fraction surfaces of samples were observed using PhilipXL39 SEM. The fraction surfaces were coated with a layer of gold about 200 Å thick.

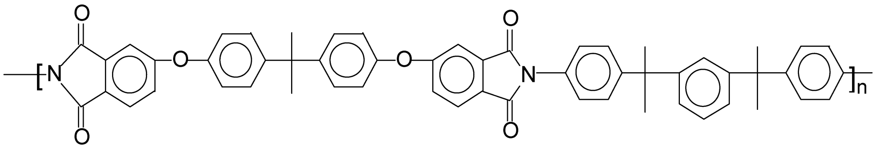

Fig. 1. Chemical structure of polyetherimide.

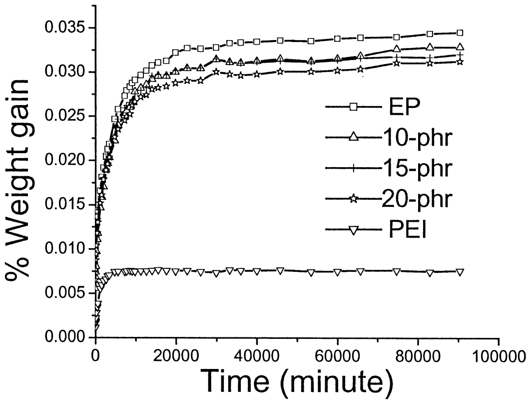

Fig. 2. Gravimetric diffusion curves.

3. Results and discussion

The sorption of water for samples with varying PEI content was investigated at 40 °C by gravimetric measurements (Fig. 2).

It appears that the behavior of these sorption curves still conforms to Fickian diffusion, and with reasonable disposals their diffusion coefficients fulfill the following equation according to Fick's second law [29].

$$\frac{M}{M_{\max}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right] \quad (1)$$

where D is the diffusion coefficient, L is the thickness of the specimen, $M_{\max}$ is the equilibrium value of the diffusing water at infinite time.

The water sorption (uptake at time t, M_t) of the sample is achieved as below:

$$M_t = (W_t - W_0)/W_0 \times 100 \quad (2)$$

where W_0 is the weight of the dry specimen, W_t is the weight of the wet specimen at time t.

Diffusion coefficients (D) acquired by non-linear curve fitting according to Eq. (1) and equilibrium water uptake (M_∞) gained from Eq. (2) is presented in Table 2.

The results shown in Table 2 indicate that addition of PEI causes a reduction in the equilibrium water uptake. While the experimental results are all higher than calculated values from additional law, which is described below:

$$\mathrm{Fv}_{\mathrm{blend}} = (\mathrm{w}\%)_x\mathrm{Fv}_x + (\mathrm{w}\%)_y\mathrm{Fv}_y \quad (3)$$

This can be clarified by the evidence that DDS is not dispatched evenly in the system [30]. Because of the low solubility of DDS in PEI, with the augment of PEI fraction, concentration of DDS in epoxy phase will go up correspondingly resulted from phase separation. Thus, the curing extent is enhanced, which will bring about an increase in the number of hydrophilic groups followed by more water absorbed.

Additionally, fractional free volume (Fv) is traditionally considered to be another major factor that predicts the water sorption process in epoxy resins [7,8,10], which is recently studied by PALS measurements [17,19–27].

We have measured the positron spectra under room temperature, and with the help of PATFIT [31], three positron lifetimes were resolved for the spectra. The shortest-lived component and the intermediate component are attribution to the self-annihilation of *para*-positronium (*p*-Ps) and the positron annihilation, respectively. The longest-lived component, with lifetime τ_3 and intensity I_3, results from the pick-off annihilation of *ortho*-positronium (*o*-Ps) in the free volume holes. According to previous papers, it is assumed that the lifetime τ_3 is proportional to free volume hole size [21] and the intensity I_3 is connected with free volume hole number [22].

Assuming that the free volume holes are spheres, the average radius R of holes and the fractional free volume (Fv) were calculated as below [19,21]:

$$\tau_3 = 1/2[1 - R/R_0 + 1/2\pi\,\sin(2\pi R/R_0)]^{-1} \quad (4)$$

where R_0 is the radius of the finite spherical potential, $R = R_0 - \Delta R$ is the radius of free volume, $\Delta R = 1.656$ Å is an empirical parameter which is obtained by fitting the measured lifetime of cavities with known size [19,21,32].

$$\mathrm{Fv} = 4/3\pi R^3 C I_3 \quad (5)$$

where C is an empirical parameter with the value of 0.0065 Å^{-3}, which is obtained from thermo-expanse results for the system studied here and cannot be used as a universal constant for other materials.

The results of PALS are listed in Table 3.

As shown in Table 3, EP has the largest *o*-Ps intensity I_3 and the shortest τ_3 while PEI is just the opposite. This phenomenon suggests that the free volume hole size in EP is relatively small, while hole number is relatively large compared with that of PEI. Attribution to the combined

Table 2
Diffusion results at 40 °C from gravimetric measurement

	EP	10-phr	15-phr	20-phr	PEI
D^a	2.62	2.89	2.88	3.04	10.00
M_∞ (%)	3.46	3.32	3.22	3.16	0.75
M_∞^{cal} (%)^b		3.26	3.18	3.10	

[a] The unit of diffusion coefficient is 10^{-8} cm^2 s^{-1}.

[b] Calculated equilibrium water uptake M_∞^{cal} is derived from additional law.

Table 3
Free volume results at room temperature from PALS

	EP	5-phr	10-phr	15-phr	20-phr	PEI
τ_3 (ns)	1.647	1.658	1.624	1.617	1.619	1.859
I_3 (%)	21.75	19.54	19.25	18.41	18.21	9.66
R (nm)	0.250	0.251	0.248	0.246	0.247	0.272
Fv (%)	0.93	0.84	0.80	0.75	0.75	0.53
Fv$^{\mathrm{cal}}$ (%)^a		0.91	0.90	0.88	0.87	

[a] Calculated fractional free volume Fv$^{\mathrm{cal}}$ is derived from additional law.

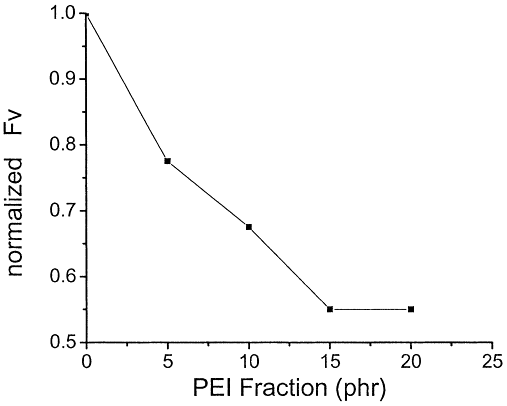

Fig. 3. Normalized fractional free volume curve.

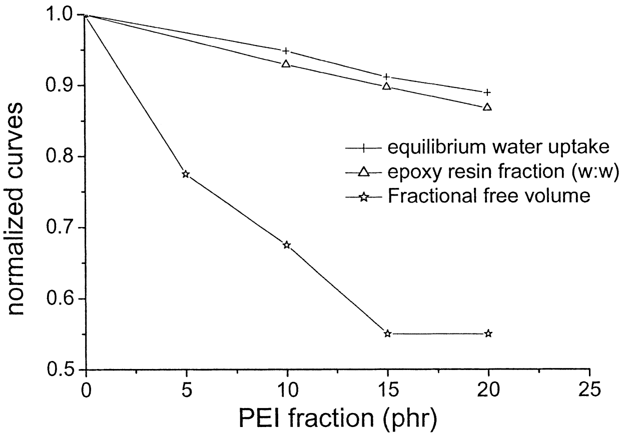

Fig. 5. Normalized equilibrium water uptake, epoxy fraction and fractional free volume curves.

effect of free volume hole size and hole number, fractional free volume decreases obviously with the increasing PEI fraction. The expected variation with component would be a linear extrapolation between the values for EP and PEI. However, the overall variation of fractional free volume is not linear, which can be seen clearly in Fig. 3.

The slope of normalized fractional free volume curve turns to be relatively smooth when the PEI fraction reaches 15 phr that almost exactly in accordance with the change of morphology from dispersed phase to co-continuous phase as shown in Fig. 4.

Obviously, the drop of the fractional free volume must be related to specific morphology, especially in case of dispersed phase for the systems studied here. In addition, the experimental results obtained from PALS are all lower than outcomes from additional law that neglects the

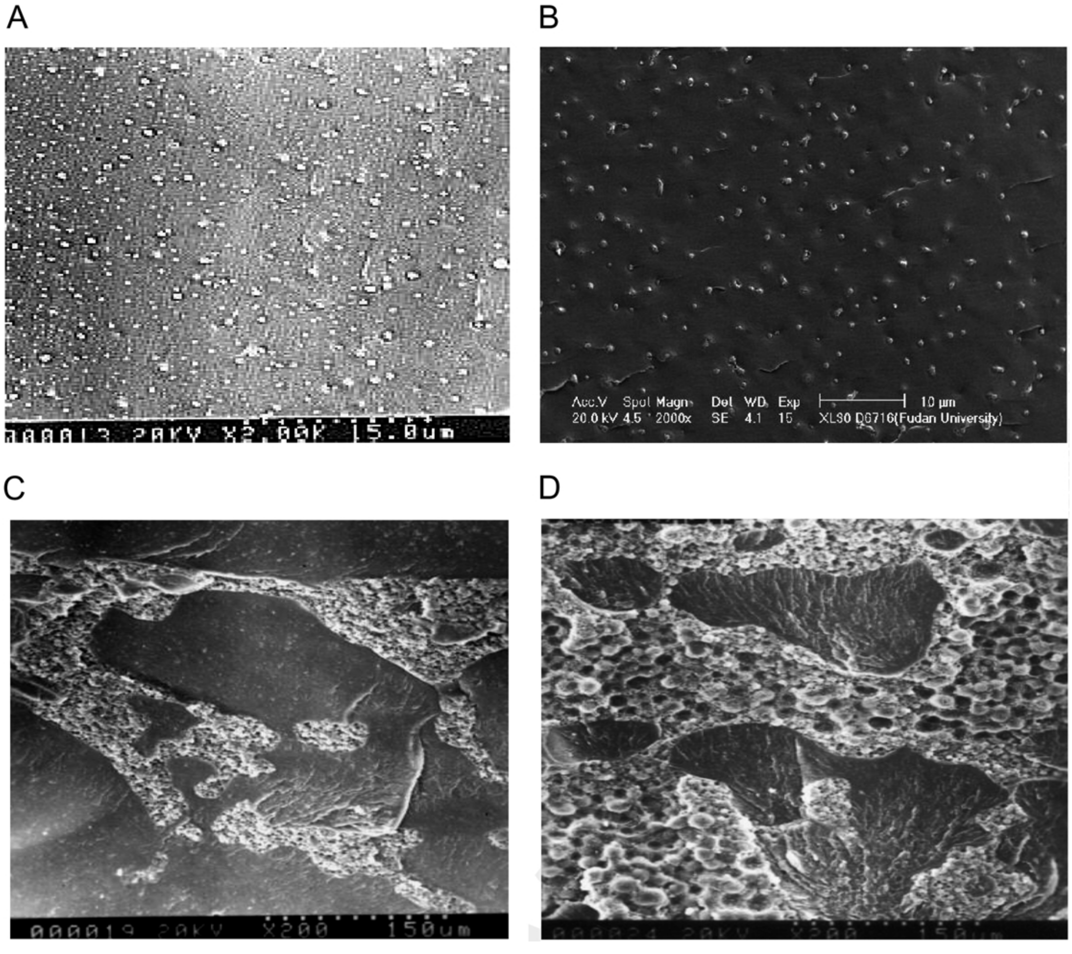

Fig. 4. The SEM phase structures: (A) 5-phr (× 2000); (B) 10-phr (× 2000); (C) 15-phr (× 200) and (D) 20-phr (× 200).

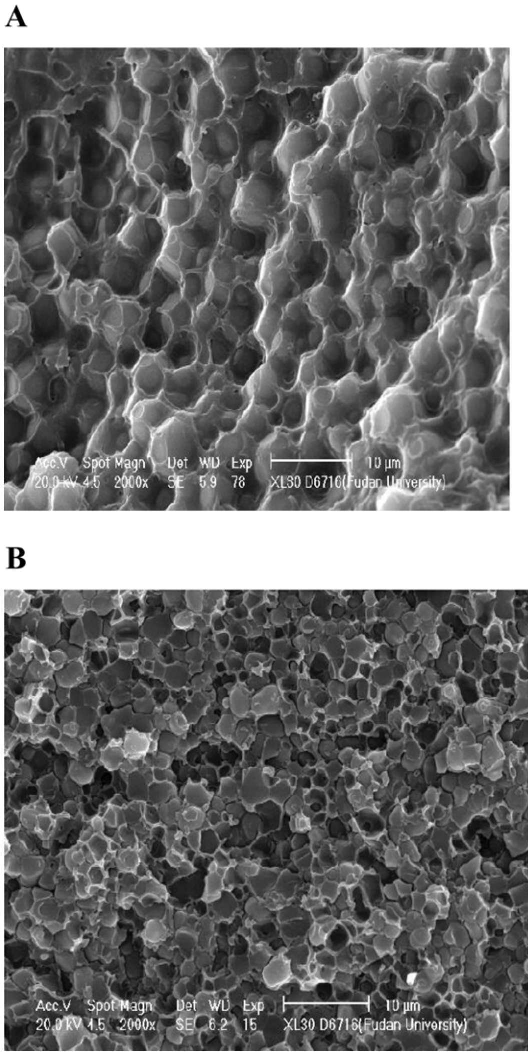

Fig. 6. SEM phase morphologies of (A) 15-phr (× 2000) and (B) 20-phr (× 2000).

morphology effect, which also supports the conclusion above. Furthermore, the fluctuation of *o*-Ps lifetime τ_3 and intensity I_3 in accordance with different morphology has been observed in RT-PS modified epoxy resins [17], which suggests the influence of morphology on fractional free volume is generally existed.

However, the relationship between fractional free volume and equilibrium water uptake seems to be insensitive. In case of 15-phr, the decrease of fractional free volume compared with the overall variation is about four times bigger than that of equilibrium water uptake. On the contrary, the strong relationship between epoxy resin fraction in the blends and equilibrium water uptake is observed (Fig. 5), which suggests that water molecules are mainly located in the epoxy regions and hydrophilic groups are more important in determining ultimate water sorption. Although the similar conclusion has been reported in different single component systems [11,25–27], it was first noticed in the blends.

Confusingly, the change of diffusion coefficients implies less composition-dependent as shown in Table 2. Pure epoxy resin has the lowest diffusion coefficient for there are numerous hydrophilic groups such as hydroxyl and amine which will strongly couple with the water molecules by hydrogen bonding so as to impede the water diffusion. But it is puzzling to find that the values of diffusion coefficient of 10-phr and 15-phr remain constant and relatively small compared with their PEI fractions. There may be two reasons here. First, an excess of hydrophilic groups introduced by aforementioned higher concentration of DDS causes a lower rate of the water absorption, which counteracts the function of PEI component. Second, phase structure also takes effect. As is known, water molecules are easy to go though PEI regions while hard to penetrate epoxy networks. For the dispersed phase (Fig. 4(A) and (B)), the continuous epoxy networks can severely reduce initial rate of water sorption, which makes the diffusion coefficient close to that of EP. While in case of co-continuous phase (Fig. 4(C) and (D)), epoxy regions are occluded and at the initial stage water molecules are able to go though PEI region, which increases the diffusion coefficient in 20-phr. However, why diffusion coefficient remains small in 15-phr is still vague. To further investigate the subtle difference in the morphology of blends, Fig. 6 is presented by amplifying the microdomains of Fig. 4(C) and (D).

Clearly, the epoxy regions occluded by PEI continuous phase are wrapped more completely for 15-phr. As a result, channels for water molecules in tightly compacted epoxy regions may be narrowed and a long percolation path between the two components may be generated, which can be proved by the fact that 15-phr has the smallest average hole radius (shown in Table 3). Thus, anomalous water behavior is observed. In addition, at the occurrence of the co-continuous phase for PES modified triglycidylamino-phenol systems, Pethrick also found the minimum of diffusion coefficient accompanied by the roughest surface [18], which nearly shared the same character as the phenomenon observed here. In general, the variation of diffusion coefficient is a reflection of the delicate balance of factors that control the final result and does not lent itself to a simple interpretation.

4. Conclusion

Increasing the PEI fraction in the blends of PEI/DGEBA has the effect of increasing the equilibrium water uptake and diffusion coefficient in the system. Gravimetric measurement, PALS technique and SEM are performed here in order to depict the key factors that govern the water absorption. Strong component-dependent of equilibrium water uptake is observed, which suggests the water molecules locate mainly in epoxy resin. In accordance with the previous work in single component systems [11,25–27], hydrophilic groups rather than free volume are more significant in determining ultimate water sorption. While anomalous diffusion behavior observed is chiefly attributed to the specific morphology, to which the volume of channels for water molecules are subjected. Particularly, morphology induced by phase separation not only has the function of decreasing fractional free volume, but changes the curing extent and the number of hydrophilic groups in epoxy rich regions as well. Thus, water sorption behavior in the blends is quite different from that in single component systems.

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