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Permeabilities of solvents through epoxy membranes prepared via chemically induced phase separation

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ABSTRACT

Epoxy membranes were prepared from epoxy resin, D.E.R. 331, and cured with 2,4,6-tris-(dimethylaminomethyl) phenol (DMP-30) in diisobutyl ketone (DIBK). It was found that either the surface or bulk morphology of the cured polymers was dependent on the solvent fraction in the reactive solution. SEM showed the surface pore size of the epoxy membranes was approximately 0.12 to 1.46 μm. It was observed that the overall porosity increases from approximately 0.38 to 0.54 by increasing the concentration of DIBK from 32 to 40 vol.% in the curing solution. Furthermore, the epoxy membranes possessing connected channels were formed via chemically induced phase separation (CIPS). The connected structure of the epoxy membrane was further confirmed by a permeation test. The permeability of the solvent was approximately 7–5700 l/m^2·hr bar, which was dependent on the porous structure, and cyclohexane had the highest permeability compared to the other solvents. The glass transition temperature of the cured epoxy membrane was higher than 110^{o}C, and good thermal stability was confirmed by thermogravimetric analysis (TGA).

Keywords: Epoxy membrane; Phase separation; Porosity; Morphology; Permeability; Thermal stability

1. Introduction

Porous polymers have been found to have many useful applications, including as separation media, foams, chromatography supports, and membranes for cell culture [1–3]. Many methods have been developed to produce different morphologies of porous polymers. Chemically induced phase separation (CIPS) is a process in which a homogeneous solution of monomers or prepolymers and solvent become phase separated during polymerization. The porous polymers are then obtained after evaporation of the solvent in the matrix by heating the sample above the glass transition temperature, T_g [4–6]. For example, macroporous epoxy networks with a narrow pore size distribution and a closed-cell morphology have been prepared from epoxy resin cured with a primary amine in the presence of hexane or cyclohexane [7,8]. It was proposed that the solvent-rich closed domains were formed via nucleation and growth. Furthermore, the pore size and distribution could be controlled by the fraction of solvent.

Because epoxy thermosets have great versatility, low shrinkage, good chemical resistance, low dielectric constant (Dk), and outstanding adhesion, the porous epoxy networks can be applied as a low Dk material or as a matrix to host another phase that contains conductive or electro-optical properties [9]. Furthermore, it has been reported that when phase separation is induced via step-wise polymerization, it is difficult to obtain bi-continuous structures from the addition of a low-molecular-weight compound, such as a solvent. In the curing system of epoxy resin with a primary amine, polymers grow mainly via a step-wise polymerization, which causes a closed-pore structure in the epoxy matrix

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[10,11]. The epoxy resin can be also cured through the use of small amounts of Lewis bases, such as tertiary amine, which act as initiators of the anionic polymerization [12,13]. It is believed that, in the presence of low-molecular-weight compounds, the morphology of polymer membranes prepared from the epoxy resin cured with tertiary amine might be different from those cured with primary amine.

In this study, 2,4,6-tris-(dimethylaminomethyl) phenol (DMP-30) was chosen as a curing agent, and the porous epoxy membranes were developed by chemically induced phase separation. The solvent permeabilities through the epoxy membranes dependent on either the morphology or the solvent are further discussed.

2. Experimental

Diglycidyl ether of bisphenol A type epoxy resin from Dow Chemical Company (D.E.R. 331, EEW=186) and the curing agent: 2,4,6-tris-(dimethylaminomethyl) phenol (DMP-30, reagent grade) from Aldrich were used without further purification. The solvent diisobutyl ketone (DIBK, molecular weight 142.2) was purchased from Acros. The epoxy resin D.E.R. 331 was mixed with DIBK and stirred to form a homogeneous solution. Then, DMP-30 was added into the mixture. The solution was transferred into a plate mold, covered, and sealed with contacting sheets coated with silicon wax or Teflon. The solution was cured at approximately 40°C for 24 h. The gelled sample was taken out of the mold and placed into a vacuum oven at 170°C for 24 h to post cure and remove solvent.

The morphology of the cured epoxy membrane was observed using a scanning electron microscope (SEM, Hitachi S-3000H). The glass transition temperature T_g of the cured samples was determined by a differential scanning calorimeter (DSC, TA 2910) with a heating rate of 10°C/min. The thermal degradation temperature was measured using a thermal gravimetric analyzer (TGA, TA Q-50) under nitrogen purge. Furthermore, the cured membrane (thickness of approximately 0.25 mm) was mounted between two steel circular rings, which had a 13 mm inner diameter. The solvent flow through the membrane was measured at room temperature and a constant pressure of 0.8 bar. Permeability was calculated by the following equation:

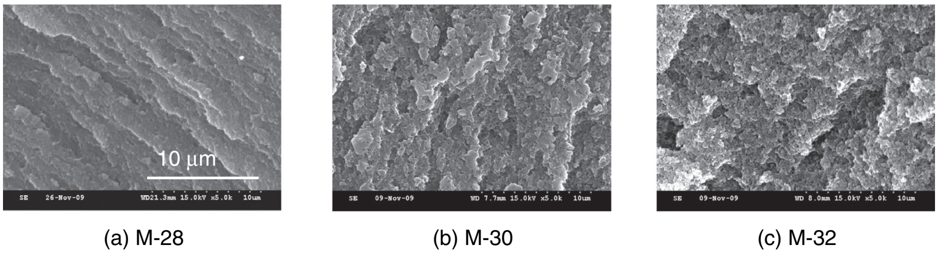
$$J' = \frac{Q}{A \cdot \Delta p} \tag{1}$$

where Q is the steady volumetric flow rate of solvent, A is the cross area of the membrane, and Δp is the pressure drop across the membrane (0.8 bar in this study).

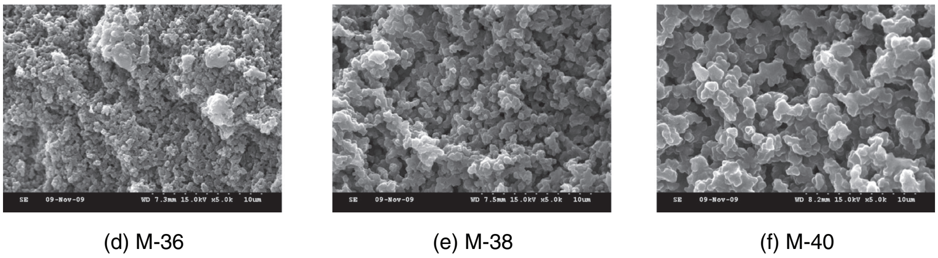
3. Results and discussion

Fig. 1 shows the SEM images of the cross-section morphologies of the cured epoxy membranes prepared under various fractions of DIBK. Sample M-28 exhibited a dense morphology, which was formed at 28 vol.% of DIBK. By increasing the solvent to 32 vol.%, a porous structure was observed. SEM images demonstrate that the polymer membranes with connected channels were formed via epoxy resin curing with DMP-30.

The surface morphology of epoxy membranes prepared under various fractions of solvent is illustrated in Fig. 2. It was found that a dense structure was formed with 28 vol.% of DIBK. However, at concentrations

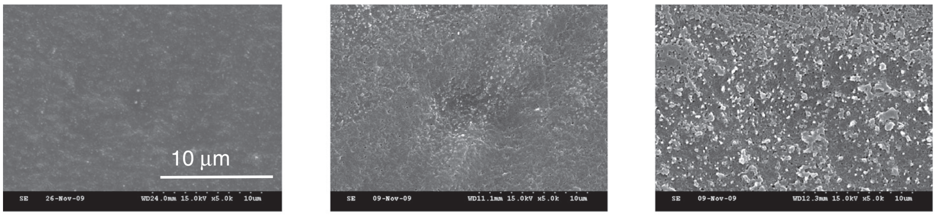


(a) M-28 (b) M-30 (c) M-32

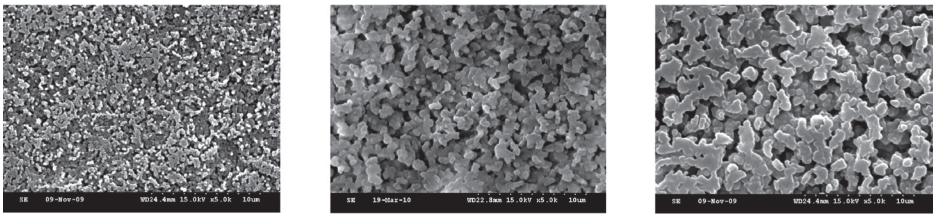


(d) M-36 (e) M-38 (f) M-40

Fig. 1. SEM images of the cross-section morphologies of epoxy membranes.



(a) M-28 (b) M-30 (c) M-32



(d) M-36 (e) M-38 (f) M-40

Fig. 2. SEM images of the surface morphologies of epoxy membranes.

higher than 32 vol.%, some pores on the surface came out. Furthermore, the pore diameter was measured by the SEM photograph, and the mean pore diameter was calculated according to

$$d_m = \sqrt{\frac{\sum n_i d_i^2}{\sum n_i}} \qquad (2)$$

where n_i is the number of pores with diameter d_i. The surface porosity is calculated by dividing the total of all the pore areas in the SEM image by the total area of the image. As seen in the SEM diagrams and in Table 1, the channel diameter and surface pore size increased with increasing DIBK. On the surface of membrane, the pore size was approximately 0.12 μm at 32 vol.% of DIBK, which increased to 1.46 μm at 40 vol.%. When the DIBK for preparing the membrane increased from 32 vol.% to 40 vol.%, the surface porosity increased from 0.08 to 0.48.

Fig. 3 indicates the different solvent permeabilities of the epoxy membranes. For example, the permeability of cyclohexane through the membrane M-40 was 5791 l/m^2·hr·bar, whereas for water and ethanol it was 3754 and 765 l/m^2·hr·bar, respectively. All membranes showed the highest permeability for cyclohexane and the lowest permeability for water. Moreover, the water could only flow through the membranes with a large porosity, such as M-38 and M-40. In both M-38 and M-40 the difference of the contact angle of cyclohexane on the membrane is small, as shown in Table 2. This implies that the cured membrane has a good affinity for cyclohexane, which results in this membrane having the highest permeability for cyclohexane compared to all other solvents. On the contrary, the cured membrane exhibits a hydrophobic property. Therefore, it is difficult for water to flow through membranes that have a low porosity.

The epoxy networks prepared from different amounts of DIBK were further investigated by DSC, the

Table 1
Pore structures of epoxy membranes

Sample*	Fraction of DIBK (vol%)	Surface mean pore diameter (μm)	Surface porosity	Overall porosity	Thickness of membrane (mm)
M–32	32	0.12	0.08	0.38	0.22
M-34	34	0.18	0.20	0.41	0.25
M-36	36	0.31	0.21	0.40	0.26
M-38	38	0.43	0.36	0.45	0.25
M-40	40	1.46	0.48	0.54	0.27

*The sample code, M-x, denotes the membrane was made from the solution with x vol% of DIBK.

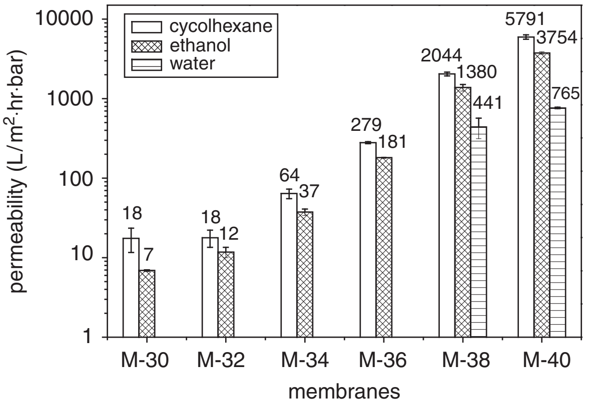


Fig. 3. Solvent permeability of epoxy membranes.

Table 2
The contact angle of the solvent on the membrane

Contact angle	cyclohexane	Ethanol	water
	14.4°	21.4°	129.4°

Table 3
The thermal properties of the membranes

Sample	T_g (°C)	T_d*(°C)	T_{max}**(°C)	Char residue at 600°C (wt%)
M-28	118	367	436	11
M-30	115	360	435	11
M-32	111	358	436	11
M-34	112	358	434	11
M-36	111	357	432	11
M-38	112	359	440	10
M-40	109	357	440	10

* Temperature at 5% weight loss under nitrogen purge at heating rate of 10°C/min.

** Temperature at maximum decomposition rate.

results of which are listed in Table 3. It was found that all glass transition temperatures, T_gs, were higher than 100°C. The T_g of the dense epoxy thermosets, M-28, is approximately 118°C and decreased from 115 to 109°C when the networks prepared from the solution with solvent increased from 32 vol.% to 40 vol.%. This result may be due to a slightly lower cross-linking density of the membrane made from the higher fraction of DIBK, which caused a lower glass transition temperature. Furthermore, the thermal decomposition of the cured epoxy networks was analyzed by TGA under nitrogen purge. The thermal properties of the epoxy membranes are summarized in Table 3. At a heating rate of 10°C/min, a 5% weight loss of the sample occurred from 357 to 367°C, and the temperature of the maximum decomposition rate was higher at 432°C. This shows that epoxy membranes with a good thermal stability can be achieved from the epoxy resin/DIBK mixture cured with DMP-30.

4. Conclusions

The polymer networks with connected channels have been prepared via the polymerization of epoxy resin with tertiary amine (DMP-30) in the presence of 32-40 vol.% of diisobutyl ketone (DIBK). The interconnection structure of the cured epoxy membranes was further verified by a solvent permeation test. It was found that the solvent permeability of the epoxy membrane was dependent on the morphology and the interaction between the solvent and membrane. Furthermore, TGA analysis showed a 5% weight loss of the cured samples at temperatures higher than 350°C. Because epoxy thermosetting membranes have performance advantages over other thermoplastic polymers, such as good chemical resistance, superior mechanical properties, reduced degradation from water ingress, and high thermal stability, it is believed that the epoxy membrane is preferable for use in separation process under severe conditions.

Symbols

d_m: Mean pore diameter, µm;
n_i: Number of pores;
d_i: Pore diameter, µm;
J': Permeability, l/m² hr bar;
Q: Steady volumetric flow rate, l/hr;
A: Cross area of the membrane, m²;
ΔP: Pressure drop across the membrane, bar.

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