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Detailed exploration of structure formation of epoxy-based monolith with three-dimensional bicontinuous structure

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Abstract

To explore a clear formation mechanism of three-dimensional (3D) bicontinuous skeleton and control the structure of epoxy-based monolith, we have prepared the monolith using a mixture of good and poor solvents. The influences of reaction and phase separation parameters, such as molecular weights and content of porogenic poor solvents, porogenic good solvent concentration, equivalent ratio of epoxy group to amine and reaction temperature on the final morphology are systematically studied by monitoring the reaction process with differential scanning calorimetry (DSC) and observing the cloud points (CP). Depending on the above parameters, the resulted morphology can be varied ranging from closed pore structure to globules aggregated structure, which was controlled by the competitive kinetics between the domain coarsening and the structure freezing. The optimized monoliths with uniform and controllable pores have a great potential application in chromatographic separation, membrane filter, and membrane emulsification.

1. Introduction

Porous polymer-based monolithic materials have important applications in these fields of foams ¹, membranes ², filters, chromatography media ^{3, 4}, and solid supports ⁵ for their good properties such as low density, good thermal and electric insulation, high specific surface area and special pore structure. Realization of each function mainly depends on special structure of porous material.

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Therefore, control of morphology has been an attractive subject. In situ polymerization was firstly applied for preparation of polymer monolith in 1990s⁶. In this approach, pores in the monolith were fabricated by phase separation between polymers and porogenic solvents induced by polymerization without stirring. The variety of porogenic solvents had a great influence on the morphology of the monolith due to the different interaction (or termed as affinity between the two phases of polymer skeleton and porogenic solvents) and different effects on the reaction rate such as polarity, hydrogen bond and viscosity. Porogenic solvents were generally classified into good and poor solvents according to their affinity with the polymer skeleton. For example, the mixture of 1-decanol and cyclohexanol was extensively used for preparation of polymer monoliths based on copolymer of methacrylate 7 or styrene 8 . In these cases, 1-decanol was poor solvent, and cyclohexanol acted as a good solvent for the polymer. The change of the ratio of these two compounds caused the shift of the pore size distribution, which was an effective method for controlling the pore diameters⁹. These morphological changes mainly resulted from the difference between reaction and phase separation rates in various porogenic solvents. Researchers have revealed that good solvent caused the delay of the phase separation and resulted in smaller pores; in contrast, poor solvent can accelerate phase separation and result in larger pores ¹⁰⁻¹².

To the best of our knowledge, the polymer monolith prepared by the free radical polymerization using the usual porogenic solvent showed a shared feature: the polymer skeleton was consisted of the connected globules due to the rapid polymerization rate. This type of structure was not favor to form large-sized object because of low strength and fragile property. Meanwhile, the formed pores in-between the globules aggregated to random and it was difficult to control pore diameters precisely ¹³. In order to avoid the heterogeneity of the monolith structure, a lot of methods were explored, for example, Aoki et al. prepared monoliths with bicontinuous skeleton structure using ultra-high molecular weight polystyrene (Mw=3050-8420 kd) as porogen to induce viscoelastic phase separation ¹⁴. Ultra-high molecular weight polystyrene solution enhanced the viscoelasticity in the polymer phase, and afforded a transient network-like morphology. In our previous study, a controlled radical polymerization for preparation of poly(methacrylate) monolith with three-dimensional (3D) bicontinuous structure was developed using methanol and hexane as porogenic solvent to moderate the phase separation rate in atom transfer radical polymerization

(ATRP) ¹⁵. In recent years, step-wise polymerization method has been studied by more and more researchers for 3D bicontinuous monoliths. Tsujioka et al.^{14, 16} proposed a step-wise polymerization method and obtained the 3D bicontinuous monolith based on epoxy resin using a single compound of polyethylene glycol (PEG) as porogenic solvent, and various influence factors on the structure of the monolith were evaluated, such as reaction temperature, monomer weight ratio, and PEG with different molecular weights. The solubility parameter of PEG had an influence on the formation of 3D bicontinuous skeleton, however, it was not the only factor that determined the exact mechanism of morphology variety; Takuya et al.¹⁷ have tried to control the structures of epoxy-based monoliths by changing the polymerization conditions such as the monomer to porogen ratio, content of the curing agent, and polymerization temperature. But they neither provided the detailed relationships between these polymerization conditions and the structures of epoxy-based monolith nor explained the reasons for the relationships. Therefore, it usually needs tedious experiments to search for the designed structure of 3D bicontinous skeleton; Jianhua Li et al. ^{18, 19} have made a serious of research to regulate the polymer structures, and found that the average pore size increased with increasing porogen concentration, increasing curing temperature, and decreasing the content of curing agent. However, these study results were only for the structure of closed pores.

In this study, to explore a clear formation mechanism of 3D bicontinuous skeleton and control the structure of epoxy-based monoliths, reaction and phase separation parameters, including porogenic poor and good solvents, equivalent ratio of epoxy group and amine, and curing temperature were varied systematically to study the impact on reaction/phase separation dynamics and final monoliths morphology. Various morphologies, such as closed pores, skeletal network, skeletal network with larger size, a mixed structure of skeletal network and globules, and globules were obtained by changing the above parameters, which was related with the competitive kinetics between the domain coarsening and the structure freezing. The corresponding relations between these parameters and morphologies were obtained and explained in detail by monitoring the reaction process with differential scanning calorimetry (DSC) and observing the cloud points (CP).

2. Experimental Section

2.1 Materials

Diglycidyl ether of bisphenol A (DGEBA, epoxy equivalent weight, EEW 199), was provided by Wuxi Resin Factory of Blue Star New Chemical Materials Co., China, with a commercial code of E-51. 4,4'-diaminodicyclohexylmethane (DDCM) was obtained from Sinopharm Chemical Reagent Co.,Ltd. PEG with molecular weight of 150.17 (PEG150), 190-210 (PEG200), 280-320 (PEG300) and 380-420 (PEG400), N,N-dimethylformamide (DMF) were bought from Beijing Chemical Factory, China. All the reagents were of analytic grade unless otherwise described.

2.2 Preparation of epoxy-based monolith

The reproducible procedure for preparation of the epoxy-based monolith was as follows (Figure 1): Firstly, a given amount of the monomer and porogens were mixed homogeneously. Wherein, the porogens were divided into good and poor solvents in this study according to the affinity between porogens and polymer chains. Then the cross-linking agent was added, and mixed uniformly. Bubbles in samples were removed by ultrasonic, and then samples were poured into a sealed mold and cured at 70 °C for 24 h. Porogens in the monolith were removed through extracting by ethanol for 24 h. Finally, samples were dried under vacuum at room temperature for 24 h.

(Insert Figure 1 here)

(Insert Table 1 here)

2.4 Determination of solvent viscosity and swelling coefficient

Solvent viscosity was measured with a Brookfield viscometer (DV- +Pro) using spindle 64 at 60 rpm and 40 °C. To assess the good solvent for the epoxy-based monolith that was synthesized without porogenic solvents, the following swelling experiments²⁰ were performed. The dried epoxy-based monolith was soaked in a given solvent for 5 h (enough time for the sheet to fully swell) at 70 °C. The swelling coefficient S was calculated according to the following formula: S (cm³/g) = $(W_{swell}-W_{dry})/dW_{dry}$, where W_{swell} and W_{dry} correspond to the weight of swollen and dried gels, respectively, and d shows the density of the solvent.

2.5 Real-time observation of the phase separation by optical microscope and SEM observation

Real-time phase separation was observed on an Olympus optical microscope (OM, LSM350,

Olympus Co., Japan) equipped with a Mettle FP82-HT hot stage. Pictures of the morphology of the sample at different curing times were taken using a WV-CP230/G camera (Panasonic Co., Japan). Scanning electron microscopy (SEM, JEM-6700F, JEOL Lim. Co., Japan) was used to observe the morphology and porous features of the samples.

2.6 Determination of reaction heat flow by DSC analysis and detection of cloud point (CP) times by light transmission

DSC (DSC7 Perkin-Elmer) was used to determine the kinetics of the curing reaction. During the curing reaction the heat flow (dH/dt) generated was measured as a function of time. Here, we need to assume that the curing rate (d α /dt) was proportional to the rate of heat flow (dH_t/dt), that was:

$$\alpha = \frac{\Delta H_{t}}{\Delta H_{t_0}} \tag{1}$$

$$\frac{d\alpha}{dt} = \frac{dH_t}{dt} \cdot \frac{1}{\Delta H_{t_0}}$$
(2)

Where α was the degree of curing; t was the reaction time; ΔH_t was the heat of reaction at time t; ΔH_t was the accumulated heat of reaction obtained during time t; ΔH_{t0} was the total heat of reaction when the reaction completed ²¹. It should be noted that the entropy not only comes from the polymerization but also comes from the phase separation. So here we make an assumption that the entropy only comes from the polymerization for the entropy movement of phase separation can be neglected when the polymerization was considered²².

The detailed procedures about DSC measurement were cleared as follows: some quality of reaction mixture was sealed in a pan, which maintained tight sealing during the measurement. The sample was heated up to the curing temperature quickly with a heating rate of 70 °C/min and then kept at curing temperature. The starting time (t=0) was set at the instant when the sample was heated up to the curing temperature. CP time determined by light transmission represented the beginnings of the phase separation process.

3. Results and Discussion

3.1 Reaction-induced phase separation

For Reaction-induced phase separation, the morphological change is attributed to the competitive occurrence of phase separation and structural freezing by gelation. The morphology with no distinct macropores obviously resulted from earlier structural freezing than the onset of phase separation. Bicontinuous structure is observed when phase separation and structural freezing almost concur with each other. When structural freezing takes place much later than the onset of phase separation, the originally bicontinuous gelling phase breaks up and becomes spherical to reduce the interfacial energy²⁰. Figure 2 was optical microscope pictures of phase separation at different time for system of E / D / dmf-0.42 / P200-2.58. It can be seen that the micro-phase separation began at 65 min. At this time, the reactive system changed into cloudy from transparent and light transmittance decreased quickly. This point was labeled as cloud point ²³, and then the phase separation proceeded in the further 10 min with a high rate. The bicontinuous skeleton was fixed at 74 min. In the next 30 min, the morphology of monolith gave no obvious change compared with the sample at 74 min. It can be seen from SEM photographs (Figure 2 g, h), there were no obvious differences between the morphologies of epoxy monoliths obtained at 74 min and 24 h respectively. These results indicated that the morphology of epoxy monolith depended on the early phase separation, while the succedent curing process had little influence. In the process of spinodal phase separation, the final morphology was determined by the competitive kinetics between the domain coarsening and the structure freezing by the curing reaction, and the evolution of phase separation might stop at any stage with reaction, which resulted in the diversity of epoxy monoliths morphology. Fast domain coarsening rate and slow structure freezing rate resulted in high phase separation degree, i.e. high dispersity of monolith structure ²⁴. Figure 3a showed that as the degree of phase separation increased, the evolution of phase structure gradually changed step by step: a. closed pores; b. skeletal network; c. skeletal network with larger size; d. a mixed structure of skeletal network and globules; e. globules.

(Insert Figure 2 here)

(Insert Figure 3 here)

3.2 Effects of porogenic poor solvents molecular weights and concentrations on the morphologies of epoxy-based monoliths

The porogenic poor solvents used in this study included PEG150, PEG200, PEG300 and PEG400. Norio et al. [20] had tried those porogenic solvents and found that PEG200 showed the best result to obtain 3D skeletal epoxy-based monolith, however, 3D skeletal epoxy-based monoliths with different size of pores also can be obtained with the other three porogenic poor solvents by adjusting the quantities of these solvents. Here, we studied the effects of the molecular weights and contents of porogenic poor solvents on the epoxy-based monoliths in detail.

(Insert Figure 4 here)

Figure 4 showed the SEM photographs of the resulted epoxy-based monolith with different molecular weight of porogenic poor solvent PEG. It can be seen that the structures of epoxy-based monoliths prepared with PEG150 and PEG200 were mixtures of skeletal network and globules (Figure 4a, b) and the other two structures prepared with PEG300 and PEG400 were skeletal network (Figure 4c, d). With the increase of porogen molecular weight, the characteristic size of pore and skeleton became smaller, which meant the degree of phase separation decreased. To explain this phenomenon, DSC curves and cloud points of systems with different types of porogens were measured. It can be seen from Figure 5a that the reaction rates gradually reduced with the increase of PEG molecular weight. This phenomenon could be explained by the differences of these solvents in viscosity (Figure 5b). High molecular weight of PEG restricted the molecular movement for the long molecular chains and hindered the collision between reaction molecules resulting in low reaction rate ^{25, 26}. The low reaction rate followed by the smaller molecular chain growth rate caused the delay of phase separation. Meanwhile porogens with high viscosity also hindered the phase separation. So the cloud points were prolonged with the increase of the molecular weight of PEG as shown in Figure 5b.

(Insert Figure 5 here)

These systems with low molecular weight of PEG as porogen have high reaction rates and fast phase separation rates according to the results of Figure 5. It was known that slow structure freezing rate and fast domain coarsening rate resulted in high phase separation degree because the final morphologies of the epoxy-based monoliths were fixed at the late phase separation stage. The resulted morphologies of epoxy-based monolith (Figure 4) indicated that these systems with low molecular weight of PEG as porogen had high degree of phase separation, i.e., larger size of phase structure. So for these systems, the fast phase separation rate played a major role instead of the high reaction rate.

(Insert Figure 6 here)

Generally, the amount of porogenic poor solvent has an important infulence on the final epoxy-based monolith morphology ²⁷. Here, we further investigated the effects of the amount of porogenic poor solvent. PEG200 was selected to complete the polymerization. Figure 6 showed the resulted epoxy-based monoliths with different contents of PEG200. The structure of epoxy-based monolith prepared with low content of PEG200 was closed pores (Figure 6a) and with the increase of porogen content, the structures changed into skeletons with increasing size of pores (Figure 6b, c, d). Figure 7a was DSC curves for systems with different contents of PEG200, which showed system of E / D / P200-2.0 had the highest reaction rate and reaction rate decreased with the increase of PEG200. The addition of PEG200 in the epoxy-amine system decreased the reaction rate by diluting the reactants ²⁸, which was consistent with the DSC results. Since the affinity of the porogen with polymer chains were the same for the same porogen, the reaction rate directly influenced the phase separation. The faster the reaction rate was, and the earlier the cloud point appeared (Figure 7b).

(Insert Figure 7 here)

Large amount of porogen decreased the system reaction rate, which caused the delay of the phase separation. But, the differences of reaction rate and cloud points of these systems with different amount of porogen were small, while the morphologies of these systems greatly changed. Because the porogenic solvent content was high, the continuous solvent-rich phase could be fully developed, which contributes to large size of pores. Phase inversion occurred when the amount of porogen was increased to a certain extent, which resulted in the globules structure (Figure 6d). So when the porogen dosage increased, the phase separation degree of epoxy-based monolith increased (Figure 6).

3.3 Effect of porogenic good solvents concentration on the morphologies of epoxy-based monoliths

Generally, porogenic solvents for epoxy-based monolith were divided into good and poor solvents

according to their affinity with the polymers. In most cases, addition of good solvents into porogen could increase the affinity of the polymer and porogen, and then change the phase separation rate ^{29,} ³⁰. In our experiment, PEG200 and DMF were evaluated by swelling experiments. According to the results of swelling experiments (Table 2), PEG200 and DMF were termed as poor and good solvents, respectively.

(Insert Table 2 here)

Good solvent in the porogenic solvents has great influence on moderating the interaction between the polymer chains and the porogen. Consequently, the amount of good solvent was an important factor on the morphology. The increased amount of the good solvent enhanced the affinity of porogens and epoxy-based monoliths. Figure 8 was SEM photographs of epoxy-based monoliths by different amount of good solvents. With the increasing amount of good solvent, pore size of monoliths decreased.

(Insert Figure 8 here)

(Insert Figure 9 here)

Degree of phase separation depended primarily on reaction and phase separation rates. The fast reaction rate shorted the phase structure evolution time which directly reduced the degree of phase separation. The small affinity between porogen and polymer chains accelerated the phase separation, and finally increased the degree of phase separation. Figure 9a showed DSC curves for systems with different good solvent contents. With the increase of good solvent, the reaction rate slightly increased. This result may be owing to the changes of viscosity caused by the addition of good solvent.

In reaction-induced phase separation, the occurrence of cloud point mainly be affected by the following two factors: Firstly, reaction rate. Only when the polymer chains were long enough, the cloud point would appear; Secondly, affinity between porogen and polymer. Good affinity inhibited phase separation, while bad affinity promoted it. From Figure 9b, it can be seen that the cloud point of E / D / dmf-0.45 / P200-2.55 was the latest, which indicated the affinity between porogen and polymer chains played a more important role than reaction rate. Thus, with the increasing amount of good solvent, the cloud points were postponed and the size of pores and skeletons decreased for the

increase of affinity.

3.4 Effects of the weight ratio of curing agent to monomer on the morphologies of epoxy-based monoliths

In reaction-induced phase separation systems with amine as curing agent and epoxy as monomer, the amount of curing agent should generally be excessive. This was caused by the phase separation which brought a large number of interfaces and the amine in the interface could not react. Only adding excess of amine, the epoxy groups could react adequately. In this study, we investigated the effects of the weight ratio of curing agent to monomers on the monolith morphology. Figure 10 was SEM photographs of epoxy-based monoliths by different weight ratio of curing agent to monomer. The size of pores and skeletons of monoliths increased with the addition of curing agent, which indicated that the addition of curing agent increased the degree of phase separation.

(Insert Figure 10 here)

Figure 11a was DSC curves with different weight ratio of curing agent to monomer. The reaction rate rose with the increase of weight ratio of curing agent to monomer. Amine functional group of curing agent had two hydrogen atoms, and the activity of the primary hydrogen was much larger than the secondary one ³¹. The large amount of curing agent can offer more primary hydrogen and improve the activity of curing reaction. When the primary hydrogen was excessive, the increase of the amount of curing agent will decrease the reaction rate because increasing the amount of curing agent will accordingly reduce the amount of monomer for the total amount of the reaction components was constant.

In Figure 11b, the cloud point appeared earlier with the increase of weight ratio of curing agent to monomer for the two systems of E-0.87 / D-0.19 / dmf / P200 and E-0.80 / D-0.26 / dmf / P200, which was because that the excessive curing agent promoted the chain-growth polymerization reaction. However, the excessive curing agent also contributed to the producing of polymer chains with few cross-linking points that have a better affinity with porogens ³². So when the curing agent was excessive enough, the cloud point would be delayed by the excessive curing agent. So the delay of cloud point occurred in system of E-0.70 / D-0.36 / dmf / P200 and the cloud point did not occur in system of E-0.64 / D-0.42 / dmf / P200, which meant that the phase separation did not start.

(Insert Figure 11 here)

The increase of weight ratio of curing agent to monomer meant the increase of primary hydrogen and the decrease of the amount of monomers, both of which would inhibited the reaction of secondary hydrogen and the generation of cross-linking points ³². So the increase of weight ratio of curing agent to monomer increased the degree of phase separation for the large proportion of polymer chains with few cross-linking points postponed the structural fixation (Figure 10).

3.5 Effects of reaction temperature on the morphologies of epoxy-based monoliths

In reaction-induced phase separation, temperature is also an important parameter because it can affect both of the reaction and phase separation rates. Figure 12 was SEM photographs of epoxy-based monoliths by different reaction temperature. The size of pores and skeletons was decreased by increasing the temperature, which was related to the reaction rate.

(Insert Figure 12 here)

Figure 13a described curves of DSC versus time for systems with different reaction temperature, and it showed that the rise of temperature increased the reaction rate. High temperature also can elevate the affinity of system which can cause the delay of the cloud point by inhibiting phase separation. However, Figure 13b showed that with high temperature, the cloud point was earlier for the higher reaction rate. So the effects of temperature on reaction rates played a dominant role. Elevated temperature accelerated the reaction rate which inhibited the process of phase separation and decreased the phase separation degree of the resulted epoxy-based monoliths.

(Insert Figure 13 here)

4. Conclusions

The morphologies of the resulted epoxy-based monoliths were determined by the competitive kinetics between the domain coarsening and the structure freezing. Low molecular weight PEG with low viscosity accelerated phase separation and resulted in large size of pores and skeletons. Large amount of porogens allowed the continuous solvent-rich phase to be fully developed, which contributed to the formation of large size of pores. The addition of good solvent into porogens improved the affinity between polymer chains and porogens and brought about small size of pores.

and skeletons for the low phase separation rate. Since polymer chains with less cross-linking points will postpone the structural fixation, an increase in pores and skeletons size was expected by increasing the weight ratio of curing agent to monomer. High reaction temperature accelerated curing reaction which brought forward the structural fixation and resulted in small size of pores and skeletons. According to the above rules, the structure of the monolith was well controlled. The resulted monoliths with various sizes of 3D bicontinuous structure have a great potential application in chromatographic separation, membrane filter, and membrane emulsification.

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	E-51/g	DDCM/g	Good solvent/g	Poor solvent/g
E /D / P150-2.3	0.75	0.25		P150(2.30)
E / D / P200-2.3	0.75	0.25		P200(2.30)
E / D / P300-2.3	0.75	0.25		P300(2.30)
E / D / P400-2.3	0.75	0.25		P400(2.30)
E / D / P200-2.0	0.75	0.25		P200(2.00)
E / D / P200-2.6	0.75	0.25		P200(2.60)
E / D / P200-2.9	0.75	0.25		P200(2.90)
E / D / dmf-0.45 / P200-2.55	0.75	0.25	DMF(0.45)	P200(2.55)
E / D / dmf-0.42 / P200-2.58	0.75	0.25	DMF(0.42)	P200(2.58)
E / D / dmf-0.39 / P200-2.61	0.75	0.25	DMF(0.39)	P200(2.61)
E / D / dmf-0.36 / P200-2.64	0.75	0.25	DMF(0.36)	P200(2.64)
E-0.87 / D-0.19 / dmf / P200	0.87	0.19	DMF(0.45)	P200(2.55)
E-0.80 / D-0.26 / dmf / P200	0.80	0.26	DMF(0.45)	P200(2.55)
E-0.70 / D-0.36 / dmf / P200	0.70	0.36	DMF(0.45)	P200(2.55)
E-0.64 / D-0.42 / dmf / P200	0.64	0.42	DMF(0.45)	P200(2.55)
E /D / dmf-0.45 / P200-2.55-T=80°C	0.75	0.25	DMF(0.45)	P200(2.55)
E / D / dmf-0.45 / P200-2.55-T=90°C	0.75	0.25	DMF(0.45)	P200(2.55)

Table 1. Starting Compositions and Sample Notations^a

^aThe reaction temperature was 70°C except these samples with special notations. In the sample notations, E , D, P, dmf represent monomers (E-51), curing agent (DDCM), poor porogenic solvent (PEG) and good porogenic solvent(DMF), respectively.

Table 2 Swelling coeffictient^a of PEG200 and DMF

	Swelling coefficient		
PEG200	0 ±0.05		
DMF	1.42±0.05		

^a All of data were the average values from three determinations. The size of samples used for experiments was about 1×1×2cm³.

Figure 1 Image of procedure to prepare epoxy-based monolith



Figure 2 Optical microscope pictures of phase separation at different time for system of E / D / dmf-0.42 / P200-2.58: (a) 64min, (b) 65 min, (c) 68 min, (d) 71 min, (e) 74 min, (f) 104 min, SEM photographs of the resulted epoxy-based monolith: (g) 74min, (h) 24h





Figure 3 SEM photographs of resulted epoxy monoliths with different degrees of phase separation: a. closed pores; b. skeletal network; c. skeletal network with larger size; d. a mixed structure of skeletal network and globules; e. globules.











Figure 4 SEM photographs of epoxy monoliths by different molecular weight of porogenic poor solvent PEG. a: E / D / P150-2.3; b: E / D / P200-2.3; c: E / D / P300-2.3; d: E / D / P400-2.3







Figure 6 SEM photographs of epoxy monoliths by different contents of PEG200: a, E / D / P200-2.0; b, E

/ D / P200-2.3; c, E / D / P200-2.6; d, E / D / P200-2.9.





Figure 7 DSC curves and cloud points of systems with different contents of PEG200

Figure 8 SEM photographs of epoxy monoliths by different contents of DMF: a, E / D / dmf-0.36 / P200-2.64; b, E / D / dmf-0.39 / P200-2.61; c, E / D / dmf-0.42 / P200-2.58; d, E / D / dmf-0.45 / P200-2.55.







contents of porogenic good solvent DMF

Figure 10 SEM photographs of epoxy monoliths by different weight ratio of curing agent to monomer: a, E-0.87 / D-0.19 / dmf / P200; b: E-0.80 / D-0.26 / dmf / P200; c: E-0.70 / D-0.36 / dmf / P200.





Figure 11 DSC curves and cloud points of systems with different weight ratio of curing agent to monomer (The cloud point of E-0.64 / D-0.42 / dmf / P200 didn't occur).

0.09

ratio of curing agent to monomer

Figure 12 SEM photographs of epoxy monoliths by different reaction temperatures: a, E / D / dmf-0.45 / P200-2.55-T=70°C; b, E / D /dmf-0.45 / P200-2.55-T=80°C; c, E / D / dmf-0.45 / P200-2.55-T=90°C.





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Figure 13 DSC curves and cloud points of systems with different reaction temperatures

(b) Cloud points of systems with different temperature