

# A Study on Formation and Stability of Epoxy Resin Inverse Concentrated Water/Oil Emulsion

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**ABSTRACT:** Inverse concentrated emulsions were prepared using aqueous colloidal silica suspension as the hydrophilic dispersed phase and a solution of diglycidyl ether of bisphenol-A (DGEBA), its curing agent polyamide resin, low molecular weight 650, surfactant nonyl phenol polyoxyethylene ether (NPE-4) in 4-methyl-2-pentanone as the continuous phase, which was expected to be used as the precursors of preparation of porous epoxy resins. The stability, i.e., the resistance to phase separation was studied. The effects of various parameters on the stability of the concentrated emulsions were investigated. The colloidal silica can strengthen the steric repulsion in the system

and improve the stability. Viscosity of both phases played a major role in the stability. Preparing of the continuous phase provided an increased initial viscosity and enhanced the stability. Lower volume fraction of the dispersed phase can help to maintain stability of the concentrated emulsions. Properly increasing the curing rate, the concentrated emulsions may acquire a high viscosity in a short time, which retarded the phase separation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 746–752, 2009

**Key words:** concentrated emulsion; epoxy; colloidal silica; stability; viscosity

## INTRODUCTION

A concentrated emulsion<sup>1</sup> is an emulsion in which the volume fraction of the dispersed phase is higher than 74%, which represent the volume fraction of the most compact spheres of equal size, and can be as high as 99%.<sup>2–5</sup> Like conventional dilute emulsions, the concentrated emulsions can also be employed as sites of reactions, with the most important one being polymerization. One of the advantages of the concentrated emulsion is that the polymerization can be carried out in either the dispersed or continuous, or both phases. If the polymerization occurs in the dispersed phase, microparticles can be obtained<sup>6</sup>; in the continuous phase, foam materials can be generated<sup>7</sup>; and in both phases, a hydrophilic–hydrophobic composite will be generated.<sup>8,9</sup>

When the volume fraction of the dispersed phase is sufficiently high, the droplets become squeezed each other, which caused an increase in free energy of the concentrated emulsion<sup>10</sup> resulting in instability. When concentrated emulsions are employed as a precursor of polymeric materials, one of the hydro-

phobic and the hydrophilic or both phases are composed of or contain monomer(s). The presence of monomers lowers the difference in polarity of the hydrophilic and hydrophobic phases and thus becomes more unstable.

The enhancement of stability becomes an important issue for the reactive emulsions. A wide variety of solid particles has been used as stabilizers of emulsions including iron oxide, hydroxides, metal sulfates, silica, clays, and carbon,<sup>11</sup> which irreversibly anchored at the oil–water interface and provide a mechanical barrier against coalescence.

In the concentrated emulsion polymerization, the increase in viscosity in either or both phases provides another mechanism for the stabilization.

As a result, the phase behavior of concentrated emulsion cannot be predicted on the basis of thermodynamic equilibrium, but on a kinetic origin. In most cases, the system will be converted to a semi-solid when the conversion exceeds a low relatively value (usually 20 wt %). For this reason, the kinetic stability of a concentrated emulsion in polymerization became a compromise between the rates of polymerization and phase separation. If the rate of polymerization is sufficiently high, the concentrated emulsion can be considered stable.

In this work, inverse concentrated emulsions of water in DGEBA were prepared, which was employed

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**TABLE I**  
The Amounts of Different Materials  
Used in the Experiment

Concentration of the colloidal silica suspension (wt %)	1, 5, 10, 15
Precuring time of continuous phase (min)	5, 30, 45, 60, 90
Volume fraction of the dispersed phase (v/v %)	74, 78, 82, 86

as a precursor of porous epoxy resins. Because of the low polarization repulsions between the 4-methyl-2-pentanone and water and the presence of other additives (polyamide resin, low molecular weight 650), the stability of the concentrated emulsion was poor. Before examining the relationship between the preparation conditions and the final structure of the product, it is instructive to carry out a study regarding the stability of the concentrated emulsions. Various parameters including the addition of colloidal silica in the hydrophilic phase, the volume fraction of the dispersed phase, the precuring of DGEBA were examined.

## MATERIALS AND METHODS

### Materials

Bisphenol-A diglycidyl ether (DGEBA, epoxy equivalent weight, EEW 228) was provided by Yueyang petroleum and chemical general plant (Yueyang, China), with commercial code of E44; polyamide resin, low molecular weight 650 was obtained from the Beijing Xiangshan combined supporting material manufacturer (Beijing, China); 4-methyl-2-pentanone was purchased from Acros Organics (Morris Plain, NJ); LUDOX TM-50 colloidal silica 50 wt % suspension in water was purchased from Aldrich Chemical Company (Milwaukee, WI); Nonyl phenol polyoxyethylene ether (NPE-4) was obtained from Beijing North Luoke Chemical (Beijing, China).

### Methods

#### Preparation of concentrated emulsions

A typical concentrated emulsion was prepared as follows. A homogeneous solution was first prepared from DGEBA (1.0 g), polyamide resin, low molecular weight 650 (0.8 g) as the curing agent, NPE-4 (0.2 g) as the surfactant, and 4-methyl-2-pentanone (1.5 mL) as the solvent. The solution was placed in a test tube (70 mL) and precured at 60°C for 30 min and used as the continuous phase. A colloidal silica suspension of 6.0 mL was added dropwise as the dispersed phase. The addition of the latter lasted about 10 min and a milky water/oil concentrated emulsion was obtained.

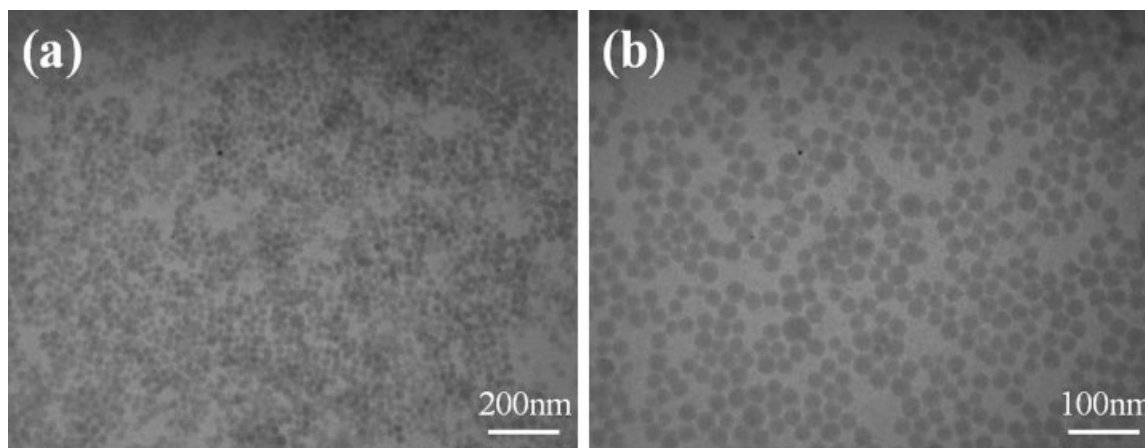
Various compositions and precuring times were employed in the experiments, which were listed in Table I.

#### Measurements

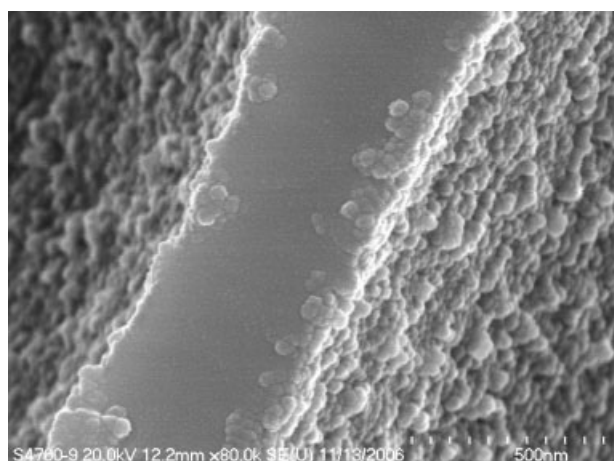
FTIR (Nicolet Nexus 670, USA) was used to evaluate the curing degree of epoxy resins. Colloidal silica suspension configuration was characterized with Transmission Electron Microscopy (HTACHI, H800-1). The morphology of semisolid concentrated emulsion was characterized using Scanning Electron Microscopy (S-4700, Jeol, Tokyo, Japan) operating at an accelerating voltage of 20 kV. The viscosity of the epoxy solutions was determined using Digital Viscometer of Agitation (Shanghai Precision and Scientific Instrument, NDJ-8S). The emulsion configuration was characterized with Optical Microscopy (BX41, Olympus, Japan).

#### Centrifugation determination of concentrated emulsion

A concentrated emulsion was introduced into a centrifuge tube sealed with rubber septa, which was



**Figure 1** Transmission electron micrographs of colloidal silica suspension. The concentration was 10 wt %.



**Figure 2** Scanning electron micrograph of a concentrated emulsion in semisolid state after being placed for 2 h at 60°C (preure time, 30 min; colloidal silica particles concentration, 10 wt %; emulsion concentration, 74%).

subjected to a mild centrifugation (1000 rpm, 1 min) at room temperature. The concentrated emulsion was separated into two phases: an upper transparent phase with a mass  $C_1$  and a milky phase with a mass of  $C_2$ . The ratio of  $C_1/C_2$  was taken as a mea-

sure of the stability of the concentrated emulsion, denoted as stability index  $K$ :

$$K(\%) = \left( \frac{C_1}{C_2} \right) \times 100\%$$

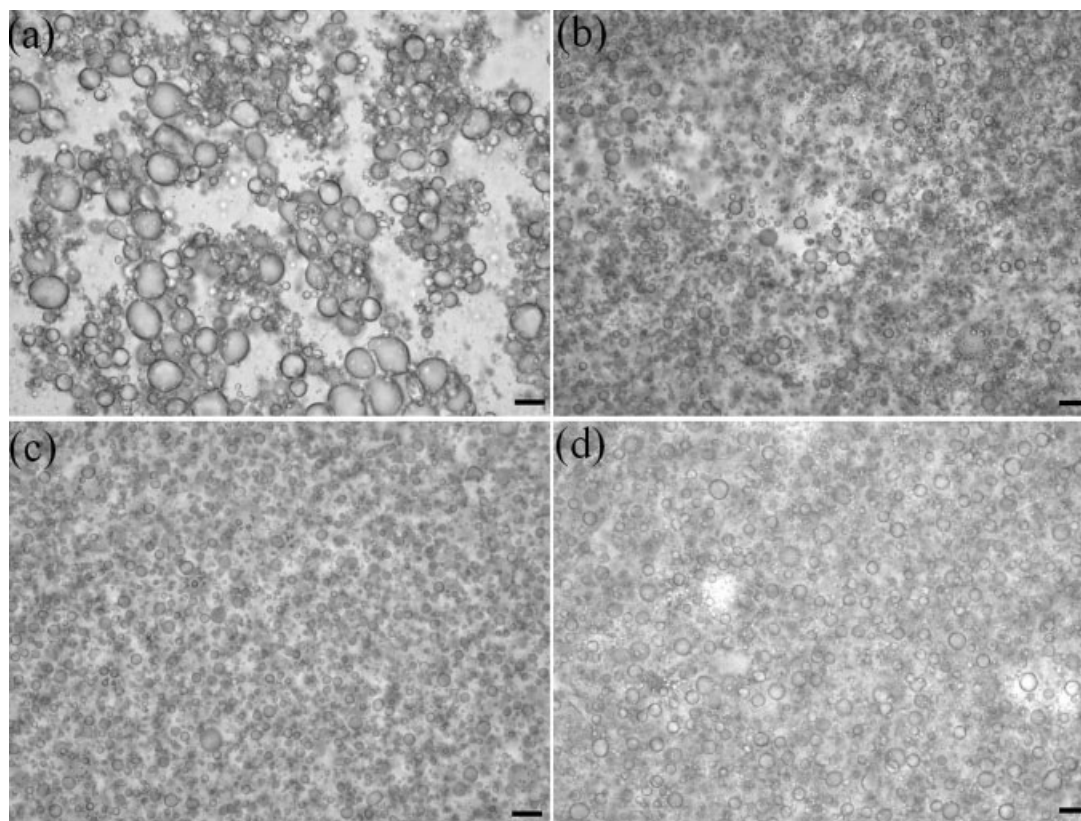
A concentrated emulsion is considered stable enough if the value of  $K$  is less than 10%.

## RESULTS AND DISCUSSION

### Influence of colloidal silica nanoparticles

Colloidal silica was introduced as an aqueous suspension into the hydrophilic phase for the following two reasons: (i) to increase the viscosity of the dispersed phase and (ii) to strengthen the steric repulsion between the two phases. The morphology of the suspension was presented in Figure 1, which showed that the colloidal silica suspended in water as nanoparticles with an average diameter of 20 nm.

When the aqueous suspension was introduced into the continuous phase, silica colloidal nanoparticles may interact with the hydrophilic ends of the surfactants through surface hydroxyl group, and thus became accumulated on the surface of the



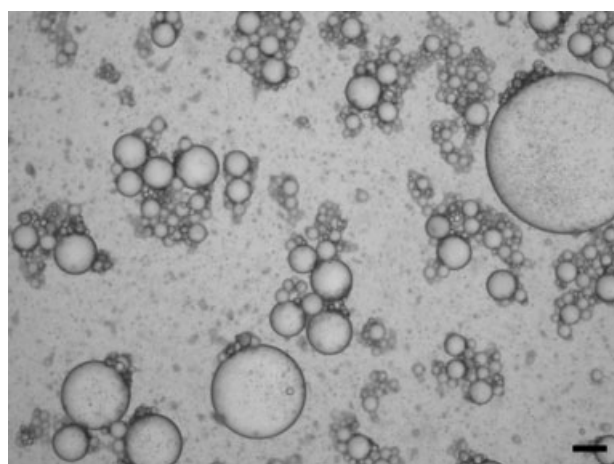
**Figure 3** Optical micrographs of concentrated emulsions with different colloidal silica nanoparticle concentrations in dispersed phase after being placed for 1 h at 60°C: (a) 1 wt %, (b) 5 wt %, (c) 10 wt %, (d) 15 wt % (preure time, 30 min; emulsion concentration, 74%). The scale bar is 10  $\mu$ m.

droplets. As a result, the hydrophilic droplets were encapsulated with a layer of colloidal silica nanoparticles.<sup>12,13</sup> The SEM micrograph in Figure 2 confirmed such morphology. The smooth strip was the continuous phase and the coarse areas are the dispersed droplets. It was clear the droplets were covered with nanoparticles. Because of the presence of the silica particles, the steric repulsion at the interface was greatly strengthened resulting in the stabilization of the concentrated emulsion. Indeed, the Figure 3 showed that a proper concentration of silica particles (about 10 wt %) in the dispersed phase may well stabilized the concentrated emulsion. If the concentration of silica particles was too low (1 wt %), serious coagulation of the droplets was observed. When the content of silica particles increased to 5 wt %, the coagulation of the droplets became negligible. However, overloading of the silica particles was not good for the uniformity of the concentrated emulsion because of the high viscosity of the suspension resulted.

#### Influence of precuring of the continuous phase

As mentioned in the introduction, the stability of concentrated emulsion has a kinetic origin instead of a thermodynamic one; the so-called stability is but a compromise between the rates of polymerization and phase separation. In this work, the continuous phase was properly precured to increase the viscosity and, more importantly, the initial conversion of the system.

Figure 4 presented an optical micrograph of a concentrated emulsion absent of curing agent. Because no curing reaction occurred both before and after



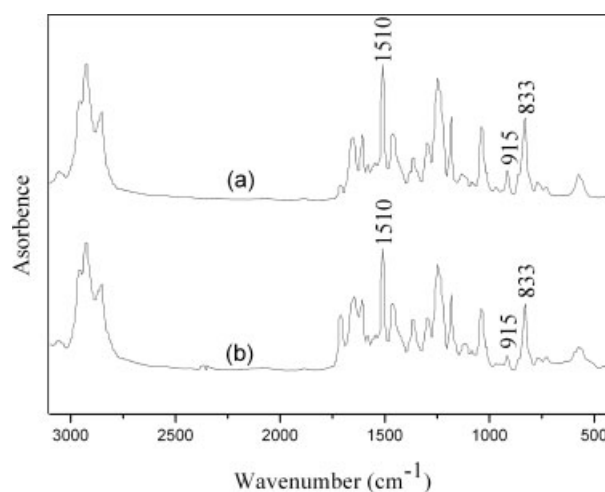
**Figure 4** Optical micrographs of concentrated emulsion absent of curing agent, the obtained emulsion is unstable and separated within 2–3 min (emulsion concentration, 74%). The scale bar is 50  $\mu\text{m}$ .

**TABLE II**  
The Viscosities of the Solutions After the Precuring for Certain Length of Time

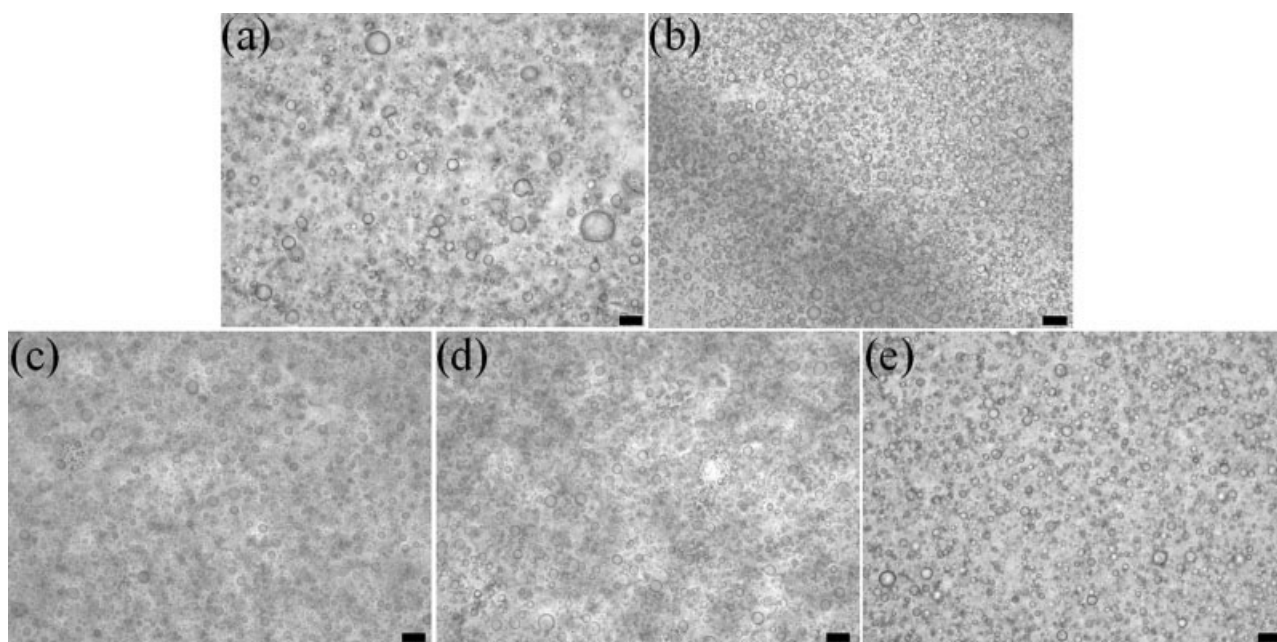
Epoxy resin (g)	Low molecular polyamide resin (g)	4-Methyl-2-pentanone	Precuring time (min)	Viscosity (Pa s)
1.0	0.8	1.5	5	0.585
1.0	0.8	1.5	30	0.739
1.0	0.8	1.5	60	0.824
1.0	0.8	1.5	90	1.106

the concentrated emulsion was prepared, the latter was extremely unstable and separated within 2–3 min. This illustrated the necessity of the precuring, because, if some curing agent were absent, the curing reaction would not be so fast to cope with phase separation within such a short time.

The increases in viscosity and degree of precuring were detected using solutions with the same composition as in the continuous phase of the concentrated emulsion. The change in viscosity of the solution was presented in Table II. It was noticed that the viscosity of the solution increased with increasing length of precuring time. This was obviously by the reactions between epoxy and amine groups resulting in extending of the molecules.<sup>14</sup> The change in functional groups was identified through FTIR spectra in Figure 5. DGEBA and polyamide resin, low molecular weight 650 during precure at different time is in Figure 5. Several peaks are identified assigned to the epoxy resin. The most important is that of the oxirane ring at  $915\text{ cm}^{-1}$ , whereas the bands at  $1510\text{ cm}^{-1}$  and  $833\text{ cm}^{-1}$  can be assigned to *p*-phenylene groups. With the increasing of precuring time, the peak of oxirane ring decreased obviously, whereas



**Figure 5** IR spectra in the wave number range  $3000\text{--}0\text{ cm}^{-1}$  obtained at different precuring time of continuous phase at  $60^\circ\text{C}$ : (a) 5 min and (b) 60 min (resin/hardener = 100/80 w/w).



**Figure 6** Optical micrographs of concentrated emulsions at different cure time of epoxy solution after being placed for 1 h at 60°C: (a) 5 min, (b) 30 min, (c) 45 min, (d) 60 min, and (e) 90 min (colloidal silica particles concentration, 10 wt %; emulsion concentration, 74%). The scale bar is 10  $\mu\text{m}$ .

the bands of the *p*-phenylene groups at 833  $\text{cm}^{-1}$  and 1510  $\text{cm}^{-1}$  remained nearly constant throughout the reaction time. Consequently, for this reason the intensity ratio of 915  $\text{cm}^{-1}$  (for oxirane ring) to either 1510 or 833  $\text{cm}^{-1}$  (for *p*-phenylene) could be taken as a measure of the concentration of the epoxy groups. Figure 5 evidenced that the consumption of the epoxy group, and thus the proceeding the curing reaction.

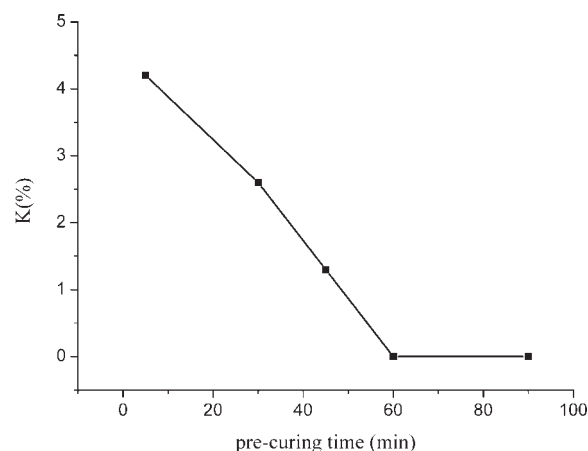
As a result of the precuring, the increased viscosity retarded the phase separation. In fact, when the conversion of DGEBA was above 20 wt %, the solution was transformed to a semisolid system and the phase separation was actually impeded. As shown in Figure 6, precuring for 30 min at 60°C was sufficient to prevent the phase separation. Longer precuring, however, caused the viscosity of the continuous phase become too high, which was harmful for the uniformly dispersion of the droplets, and larger droplets were observed in the system.<sup>15</sup> The improvement in the stability of the concentrated emulsions can also be observed in Figure 7, which showed that the stability index *K* decreased with increasing precuring time. When the precuring time was longer than 45 min, no phase separation occurred during the centrifugation indicating the concentrated emulsions were stable enough.

From the above results, one may see that the thickening of the continuous phase only retarded the separation of the concentrated emulsions, the thermodynamic nature of instability was not changed. However, the kinetic stability of the concentrated

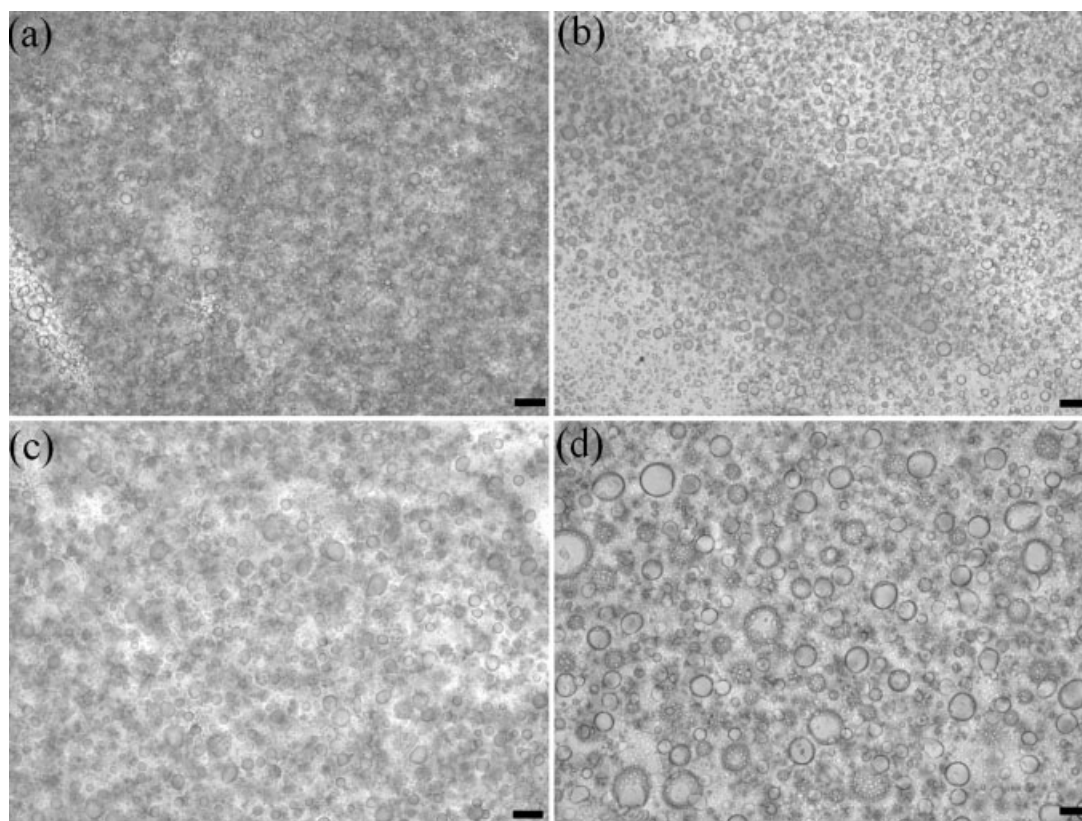
emulsions may ensure the polymerization completed in the template.

#### Influence of volume fraction of the dispersed phase

When the volume fraction of the dispersed phase is above 0.74, the droplets, assuming monodispersed, is no longer spherical, but become polyhedral. Because of the squeeze forces among the droplets, the larger the volume fraction of the dispersed phase, the greater the tendency of coagulation, and the concentrated emulsion becomes more unstable. The morphology of the concentrated emulsions with



**Figure 7** The relationship of emulsion stability index *K* and precuring time of epoxy solution.



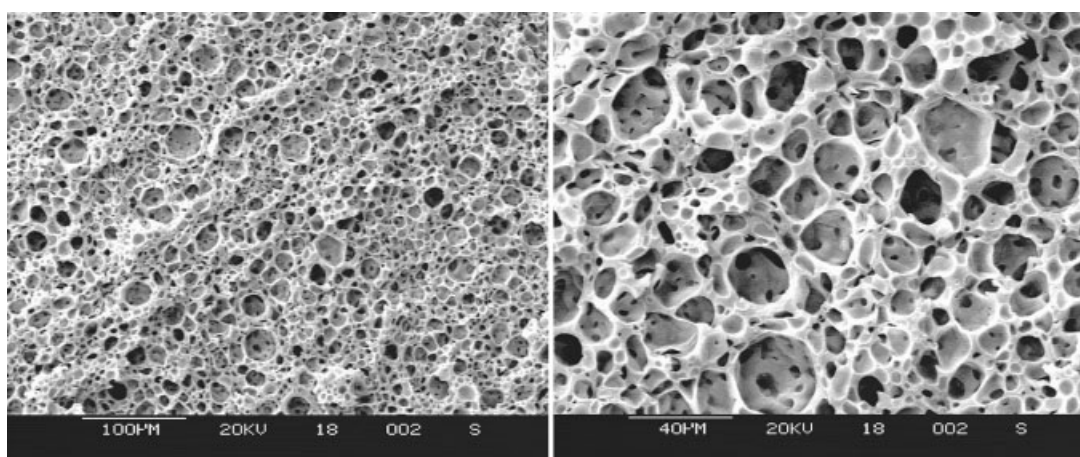
**Figure 8** Optical micrographs of concentrated emulsions at different dispersed phase volume ratio after being placed statically for 1 h: (a) 0.74, (b) 0.78, (c) 0.82, (d) 0.86 (colloidal silica particles concentration, 10 wt %; precure time, 45 min). The scale bar is 10  $\mu\text{m}$ .

different volume fraction of the dispersed phase was compared in Figure 8. It was obvious that the higher the volume fraction of the dispersed phase, the more serious the droplets coagulation.

In addition, the increase in the volume fraction of the dispersed phase caused increases in the total area of the interface, and the amount of surfactants

and nanoparticles per unit interface area will be reduced. This constituted other reasons for the poorer stability of the concentrated emulsion with higher volume fraction of the dispersed phase.<sup>16</sup>

A concentrated emulsion with high stability capability was placed into a water-bath at 60°C for 8 h to carry out the curing of DGEBA. An epoxy monolith



**Figure 9** Scanning electron micrographs of DGEBA porous monolith with different magnifications (colloidal silica particles concentration, 10 wt %; precure time, 45 min; emulsion concentration, 74%).

with porous structure could be obtained after drying, as shown in Figure 9.

### CONCLUSIONS

Inverse concentrated emulsions were prepared using aqueous colloidal silica suspension as the hydrophilic dispersed phase and a solution of DGEBA, its curing agent polyamide resin, low molecular weight 650, surfactant nonyl phenol polyoxyethylene ether in 4-methyl-2-pentanone as the continuous phase. Without colloidal silica in the aqueous phase and the precuring of the continuous phase, the stability of the concentrated emulsion was poor. The colloidal silica tended to accumulate on the surface of the dispersed droplets forming an encapsulation, which strengthened the steric repulsion in the system and thus improved the stability. Viscosity of both phases played a major role in the stability. Precuring of the continuous phase provided an increased initial viscosity and enhanced the stability. Higher the volume fraction of the dispersed phase, the lower the stability of the concentrated emulsions.

### References

1. Ruckenstein, E. *Adv Polym Sci* 1997, 127, 1.
2. Solans, C.; Pinazo, A.; Calderó, G.; Infante, M. R. *Colloids Surf A* 2001, 176, 101.
3. Tai, H.; Sergienko, A.; Silverstein, M. S. *Polymer* 2001, 42, 4473.
4. Maekawa, H.; Esquena, J.; Bishop, S.; Solans, C.; Chmelka, B. F. *Adv Mater* 2003, 15, 591.
5. Esquena, J.; Sankar, G. R.; Solans, C. *Langmuir* 2003, 19, 2983.
6. Sun, F.; Ruckenstein, E. *J Appl Polym Sci* 2003, 48, 1279.
7. Wang, X.; Ruckenstein, E. *Biotechnol Bioeng* 2004, 42, 821.
8. Sun, F.; Ruckenstein, E. *J Membr Sci* 1995, 99, 273.
9. Li, X.; Zhang, C.; Du, Z.; Li, H. *J Colloid Interface Sci* 2008, 323, 120.
10. Solans, C.; Esquena, J.; Azemar, N. *Curr Opin Colloid Interface Sci* 2003, 8, 156.
11. Binks, B. P. *Curr Opin Colloid Interface Sci* 2002, 7, 21.
12. Aveyard, R.; Bink, B. P.; Clint, J. H. *Adv Colloid Interface Sci* 2003, 100–102, 503.
13. Arditty, S.; Schmitt, V.; Giermanska-Kahn, J.; Leal-Calderon, F. *J Colloid Interface Sci* 2004, 275, 659.
14. Karaynnidou, E. G.; Achilias, D. S.; Sideridou, I. D. *Eur Polym J* 2006, 42, 3311.
15. Butler, R.; Hopkinson, I.; Cooper, A. I. *J Am Chem Soc* 2003, 125, 14473.
16. Tcholakova, S.; Denkov, N. D.; Ivanov, I. B.; Campbell, B. *Adv Colloid Interface Sci* 2006, 123–126, 259.