# Macroporous Epoxy Networks via Chemically Induced Phase Separation

**J. Kiefer,[†] J. G. Hilborn,[*,†] J. A. E. Månson,[‡] and Y. Leterrier[‡]**

*Materials Department, Polymers Laboratory, and*
*Laboratory of Composites and Polymers Technology,*
*Swiss Federal Institute of Technology, Lausanne,*
*CH-1015 Lausanne, Switzerland*

**J. L. Hedrick**

*Almaden Research Center, IBM Research Division,*
*650 Harry Road, San Jose, California 95120-6099*

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Epoxy resins are one of the most important classes of thermosetting polymers and are widely used in applications for high-performance adhesives and matrix resins for advanced composite materials.[1−4] If the network structure is properly generated, the resulting combined properties of high modulus and strength make the materials suitable for these applications. However, in contrast to such desirable properties, epoxy networks are brittle and display low fracture toughness. Many studies have been conducted on the impact modification of epoxy resins by the incorporation of a second component.[5−12] Functionalized elastomeric modifiers such as the amine- or carboxyl-terminated acrylonitrile−butadiene copolymers are the most commonly used materials. In such a strategy, one must define such parameters as solubility parameter, molecular weight, and concentration of the elastomeric component to obtain the desired level of phase separation with good interfacial bonding. The presence of these rubber particles, which typically have a diameter of 0.5−5 $\mu$m, leads to significant improvement in fracture toughness. In such systems, the phase separation is not complete and the matrix contains dissolved elastomer, resulting in plasticization and a lowering of $T_g$. Alternatively, thermoplastic polymers have also been used to enhance the toughness of epoxy resins.[13−15] The main mechanisms thought to be responsible for energy absorption in these epoxy composite systems include localized shear yielding and internal cavitation or interfacial debonding of the rubber particles, and these proposed mechanisms are triggered by different types of stress concentrations.[16,17] The cavitation of the rubber is equivalent to generating a series of voids, which would greatly reduce the degree of triaxial stresses acting in the matrix. Kinloch and co-workers have shown that this will lead to a considerable increase in the Von Mises stress in the epoxy matrix, leading to extensive plastic deformation.[18,19] To this end, Kinloch and co-workers have demonstrated that dispersed cavities toughen an epoxy network; however, the generation of the voids was difficult, leaving debonded rubber particles inside.

The most common route to produce porous polymers is by gas nucleation, where a polymer is charged with a gas-blowing agent such as carbon dioxide or nitrogen and heated to $T_g$ to nucleate and grow the gas bubbles. The high diffusion constant of the gas precludes the control of the pore size, and foams with high porosities are usually obtained.[20] Alternatively, foams have been prepared using a technique known as "thermally induced phase separation" (TIPS).[21] This technique involves the use of suitable solvent or cosolvent mixtures to induce phase separation in a polymer solution through a temperature quench. The solutions are then frozen and essentially freeze-dried to produce a foam of the initial polymer. Since, in most instances, the phase separation proceeds via a spinodal decomposition mechanism, this technique provides only high porosities and is limited to thermoplastic polymers. One of the few reports on the generation of porosity in epoxy resins was based on the preparation of a two-phase structure, where the dispersed phase was designed to be thermally labile. Amine functional propylene oxide oligomers were used to modify an epoxy resin.[22] Once cured, the propylene oxide discrete phase could be removed by a thermal treatment, generating pores. This technique appears to be limited to thin films, and attempts to extend this voiding procedure to other thermosetting resins was largely unsuccessful.

Recently, Fréchet has reported an improved method for the preparation of porous cross-linked polystyrene beads prepared via suspension polymerization.[23] The porosity was introduced through the use of a polymeric "porogen", which is miscible in the styrene monomer and phase separates as the molecular weight increases. The porogen is later extracted, leaving behind pores. Although there are numerous methods to generate porous materials, few provide moderate porosity (i.e., <30%) in a cross-linked material.

The objective of this work is to establish a general methodology to synthesize porous cross-linked polymers with controlled porosity and pore size. The strategy we sought to employ is based on the generation of a two-phase morphology via chemically induced phase separation, where the dispersed phase consists of a nonreactive low molecular weight liquid having a low boiling point. The judicious choice of the low molecular weight liquid is critical as the low molecular weight liquid must be a moderately good solvent for the reactive monomers, yet a nonsolvent for the cured network. After phase separation, the liquid phase should be removable by heating the sample above $T_g$ to allow diffusion and evaporation to generate the porous structure. In this approach, phase separation via spinodal decomposition should be avoided, as the resulting cocontinuous morphology would lead to undesirable mechanical properties. Phase separation which proceeds via a nucleation and growth mechanism would be desirable for the formation of a closed-cell porous morphology. In this approach, however, it should be avoided to ever reach a solvent concentration where phase inversion occurs.

To demonstrate the feasibility of this approach, hexane and cyclohexane were surveyed as the low molecular weight liquids to modify epoxy networks derived from the diglycidyl ether of Bisphenol-A and 2,2′-bis(4-aminocyclohexyl)propane (Scheme 1). In order to prevent solvent loss during the cure, the samples were fabricated in sealed ampules.[24] Homogeneous solutions were obtained in each case after slight heating and agitation. The samples were cured in an oven. The solvent composition ranged from 5 to 50 wt %. When cured at 80 °C, the cyclohexane-modified networks became opaque at a cyclohexane content above 16 wt %, indicative of phase separation. Calorimetry measurements showed two transitions characteristic of a phase-separated morphology. The first transition is a melting endotherm at 8 °C, commensurate with the melting point of cyclohexane. The second transition is

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[*] To whom correspondence should be addressed.
[†] Polymers Laboratory.
[‡] Laboratory of Composites and Polymers Technology.

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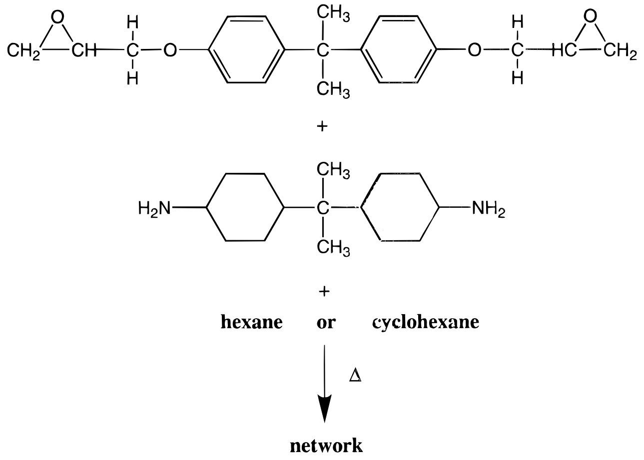
**Scheme 1. Principle of Chemically Induced Phase Separation for the Preparation of Macroporous Epoxy**



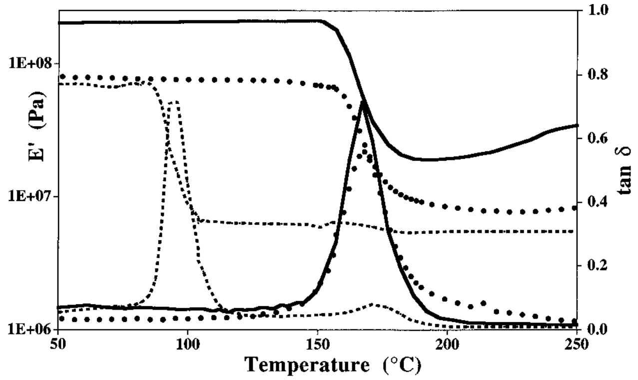


**Figure 1.** Dynamic mechanical behavior of epoxy networks prepared via CIPS with 20 wt % cylohexane prior to (- - -) and after (···) the drying compared to the neat matrix (—).

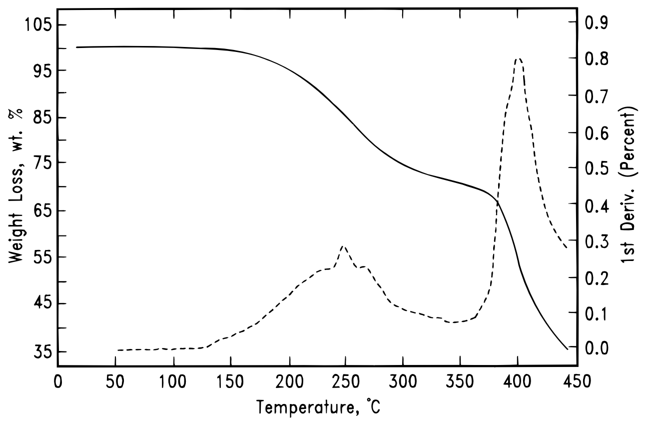


**Figure 2.** Thermogravimetric analysis of epoxy networks containing 30% cyclohexane.

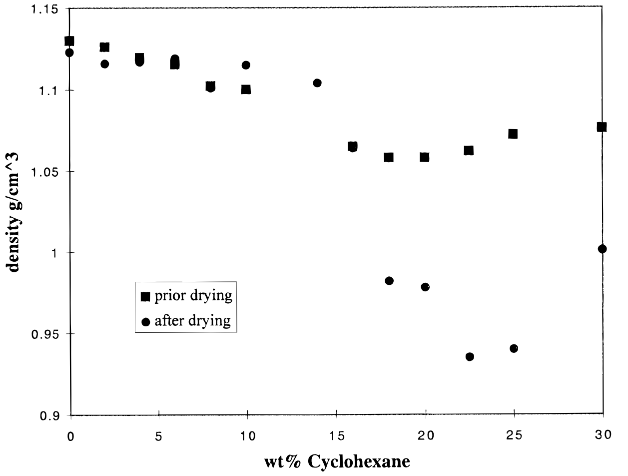


**Figure 3.** Density of dried and undried epoxy networks containing various concentrations of cyclohexane.

due to the $T_g$ of the epoxy network observed in the proximity of 120 °C and drops with cyclohexane composition. The $T_g$ of the epoxy network in the composite is lower than that of the neat epoxy, suggesting partial solubility of cyclohexane in the matrix, analogous to the rubber-toughened epoxies. The DMA results clearly show the plasticizing effect of the cyclohexane after the phase separation. After the thermal treatment, to generate the porous structure, the $T_g$ of the fully cross-linked matrix is reached (Figure 1). As expected, the moduli of the macroporous epoxies are lower compared to the neat matrix. The cure temperature of the hexane-modified networks was limited to 40 °C to maintain homogeneous mixtures. The samples became opaque at compositions as low as 7 wt %, and the thermal characteristics of the networks are comparable to those described above.

The generation of the foam was accomplished by subjecting the epoxy networks to a thermal treatment in vacuum to remove the hexane or cyclohexane. Shown in Figure 2 is the thermogravimetric analysis of an epoxy network containing 30% cyclohexane. Clearly, temperatures above the $T_g$ of the network are required to facilitate solvent removal. Foam formation was accomplished by heating at 200 °C in vacuum for 5 days to quantitatively remove the solvent and further effect network formation. In Figure 3, the density of networks is shown both before and after drying. A significant drop in density was observed for the dried samples which were opaque and initially contained 16% or more of cyclohexane. However, from these data, it appears that the volume fraction of voids or porosity is lower than the volume fraction of cyclohexane in the undried network. Therefore, only part of the solvent leads to foam formation. There are several possible contributing factors for this phenomenon. The thermal analysis clearly indicates dissolved solvent in the matrix that causes plasticization and is not involved in the formation of dispersed domains. Furthermore, partial collapse in the foam structure may have occurred above $T_g$ in spite of the highly cross-linked structure. Conversely, the samples which were observed to stay transparent upon cure showed no substantial drop in density after an identical drying procedure. In contrast to rubber-modified epoxies, these porous materials showed no reduction in $T_g$.

While the density measurements showed that the generation of a porous morphology had been successfully achieved, no information was provided on the size of the pores. To address this issue, scanning electron microscopy (SEM) was carried out on surfaces prepared by fracturing the samples with a razor blade after immersion in liquid nitrogen. In order to avoid plastic void growth, fracturing should be realized at low temperatures.[25] However, image analysis on these highly cross-linked thermosets releaved no difference in pore size and distribution, if identical samples were fractured at room temperature or in liquid nitrogen. Figure 4 shows two SEM micrographs of the porous networks which initially contained different compositions of cyclohexane. From these micrographs, it is evident that a well-defined porous structure is obtained, with spherical pores hav-

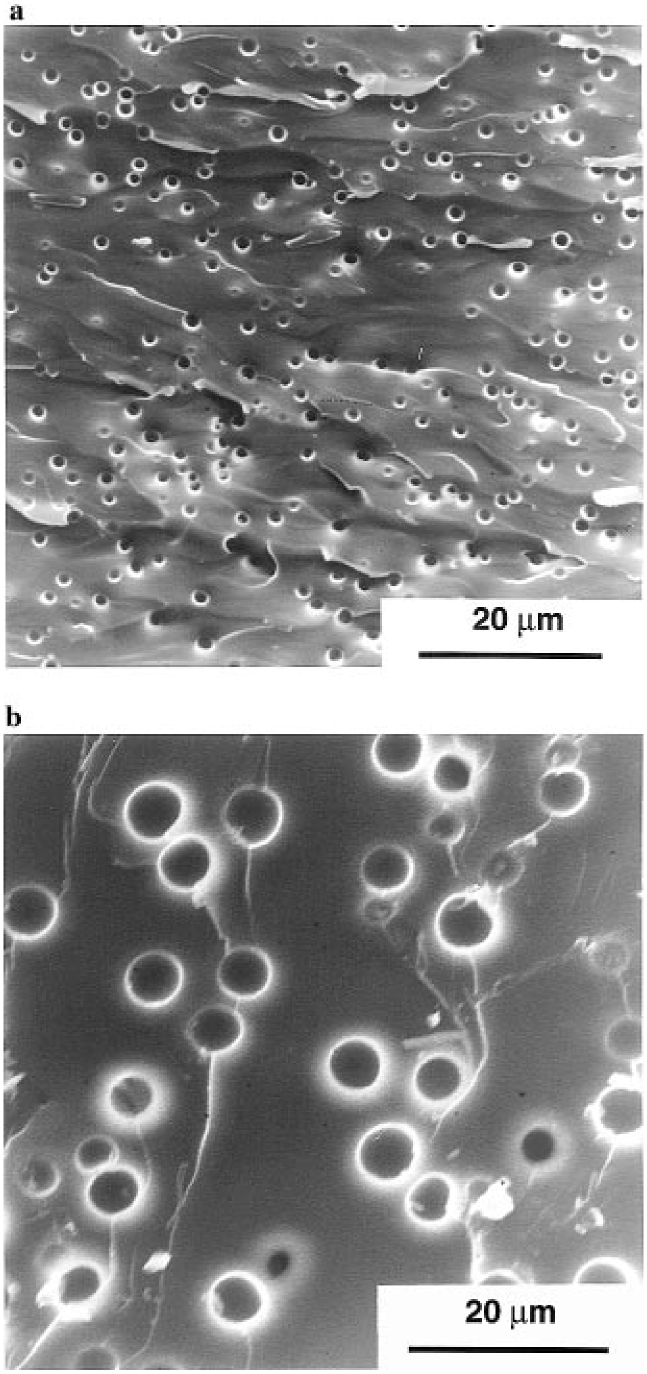


**Figure 4.** SEM micrographs of porous epoxy networks prepared with (a) 16 wt % cyclohexane and (b) 20 wt % cyclohexane.

ing a narrow size distribution in the micrometer range and pore sizes which increase with cyclohexane composition. It is also clear that no interconnectivity exists between the pores and that the desired morphology has been achieved. The size scale of the phase separation is comparable to that observed for the rubber-modified networks and is initiated by the change in free energy upon curing (i.e., the increase in molecular weight). Thus, the morphology will be a result of the competing effects between the nucleation and growth of the second phase and network conversion. Furthermore, as the solvent content increases, the pore size increases further, supporting a nucleation and growth mechanism.

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