Macromolecules **1996,** *29,* 8546−8548

Microporous Cyanurate Networks via Chemically Induced Phase Separation

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Received July 2, 1996
Revised Manuscript Received September 19, 1996

High-performance polymers play an important role as insulating materials and structural resins in manufacturing microelectronic devices and components. The material requirements for these applications generally include high thermal and dimensional stability, low thermal expansion coefficient, and low dielectric constant. A low dielectric constant is of particular importance since propagation delay of electronic signals varies with the inverse of the square root of the dielectric constant and allows for denser wiring at acceptable cross-talk noises.[1] Highly cross-linked networks possess many of the requisite properties for these applications, and epoxy resins are among the most commonly used thermosetting polymers due to their cost, availability, and ease of processing. However, drawbacks associated with epoxy networks include limited utility in applications which require high temperature and their relatively high dielectric constant values (3.8−4.5). Alternatively, cyanate ester resins, an emerging class of high-performance thermosetting polymers, have low dielectric constants (2.6−3.2), high T_g's, and high thermal stabilities. Therefore, these networks are being used in multichip modules (MCM), high-performance circuit boards, thin film cards, and direct chip attach applications. However, due to the highly cross-linked structure, they are inherently brittle, limiting their utility in applications requiring high mechanical strength or thermal cycle resistance.

There have been many studies on increasing the toughness of epoxy and cyanate resins by the incorporation of a second rubbery or thermoplastic component.[2−10] For the case of the cyanate resins, thermoplastics are the most commonly employed modifiers, presumably due to the enhanced thermal stability required for the high-temperature cure. The resulting composites produce significant improvements in fracture toughness. Although these strategies yield thermosets with improved toughness, it is often at the expense of the desired electrical properties. An alternative approach to improve the fracture toughness while lowering the dielectric constant is to generate a foam structure.[11−13] Kinloch and co-workers[14,15] have shown that microvoids in an epoxy network $\sim$1 μm in size with a volume fraction of $\sim$17% gave a significant increase in toughness. In this case, the microvoids were formed in a rubber-toughened thermoset, where the differential thermal strains cause the rubbery domains to be debonded from the matrix or internally cavitate to produce microvoids. The cavitation reduces the degree of triaxial stresses acting in the matrix, allowing extensive plastic deformation. Furthermore, a reduction in dielectric constant is realized simply by replacing the polymer with air which has a dielectric constant of 1.

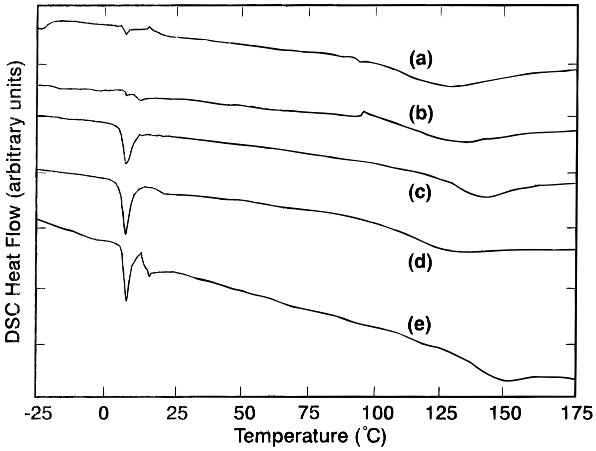

Figure 1. DSC thermograms of the composites containing (a) 10, (b) 15, (c) 16, (d) 20, and (e) 17.5 wt % cyclohexane.

Although there are numerous methods to generate porous materials, few provide moderate porosity in a cross-linked material. The most noteworthy example, reported by Frechet and co-workers,[16] is the preparation of porous cross-linked poly(styrene) beads via a suspension polymerization. The porosity was introduced through the use of a porogen, which is miscible in the styrene monomer and phase separates as the molecular weight increases. The porogen is later extracted, leaving behind empty pores. We have established a similar general methodology to obtain porous cross-linked polymers with controlled porosity and pore size.[17,18] The strategy employed is based on the generation of a two-phase morphology, where the dispersed phase mainly consists of a nonreactive low molecular weight liquid having a low boiling point. The low molecular weight liquid phase can be removed by heating the sample in the proximity of T_g to generate the porous structure. In this approach, a phase separation process is required which generates a closed-cell porous structure. High solvent contents where phase inversion occurs should be avoided also. Previously, the generation of porous epoxy networks having pore sizes of $\sim$5 μm and porosities of $\sim$20% using either hexane or cyclohexane as the nonreactive liquid was demonstrated. Recently, we have been extending this approach as a route to porous cyanurate networks. In this paper, we will describe the choice of nonreactive solvent, curing conditions to effect network formation of the poly(cyanurate), phase separation, and porosity characterization, with the objective of extending the scope of porous thermosets that can be prepared by this technique.

The cyanurate resin chosen for this study is Bis-E cyanate ester resin (ARO Cy L-10 from Ciba Geigy), since it is a low-viscosity liquid and easy to handle. The choice of the organic liquid is critical, as it must be a moderately good solvent for the reactive cyanate monomer, yet poor for the fully cured network. Cyclohexane was surveyed as the low molecular weight liquid to modify cyanurate resin, and in order to prevent solvent loss during cure, samples were cured in sealed ampules. Homogeneous solutions were obtained for cyclohexane compositions up to 20 wt %; higher compositions produced hazy solutions even when heated to 70 °C. Network formation was effected thermally and catalyzed with Bisphenol-E and 100 ppm of cobalt acetylacetonate.[19] This catalyst combination allowed a low

S0024-9297(96)00960-6 CCC: $12.00

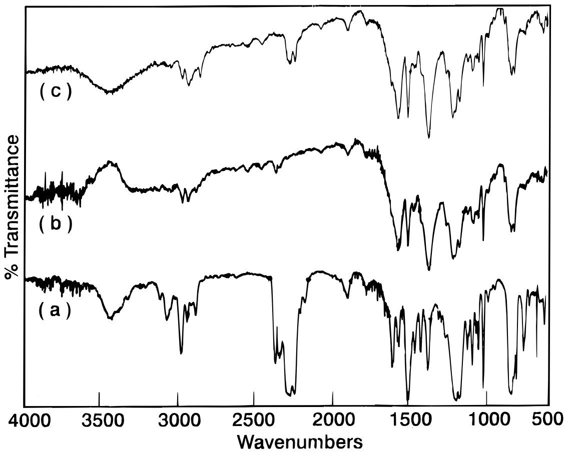

Figure 2. FT-IR spectra (a) bis-E cyanate ester resin, (b) 80 °C precure of bis-E cyanate ester resin containing 20 wt % cyclohexane , and (c) cured and dried cyanurate network.

Table 1. Density Column Data for Cyclohexane-Modified Polycyanurates Prior to and after the Drying Procedure

wt % cyclohexane	density prior to drying (g/cm^3)	density after drying (g/cm^3)
0	1.16	1.15
10	1.137	1.14
15	1.139	1.137
16	1.10	0.97
17.5	1.11	1.03
20	1.11	1.07

cure temperature (80 °C) which was found to be necessary to obtain well phase-separated samples. Higher cure temperatures produce inhomogeneous samples. The solvent compositions ranged from 5 to 20 wt %. The networks cured at 80 °C became opaque at cyclohexane compositions of 16% and above. Samples containing 15 wt % and less cyclohexane remained transparent, and no evidence of phase separation could be found by scanning electron microscopy (SEM). Shown in Figure 1 are the DSC thermograms of the composites containing 10−20 wt % cyclohexane. Clearly visible at cyclohexane compositions of 16 wt % and above is the melting endotherm (~8 °C) of the cyclohexane which can be observed along with the T_g of the partially cured cyanurate network (~125 °C), indicative of a phase-separated morphology. Furthermore, the melting enthalpy increases with cyclohexane content, consistent with a phase-separated structure. In contrast, the melting endotherm of the cyclohexane was not observed for those composites comprising less than 16 wt % cyclohexane, commensurate with a homogeneous morphology. Shown in Figure 2 are the FT-IR spectra for the cyanurate resin, partially cured resin (80 °C), and fully cured resin. Once cured to 80 °C, "B-staged", significant triazine formation (1565 cm^{-1}) can be observed at the expense of the cyanate doublet (2260 and 2250 cm^{-1}), consistent with calorimetry measurements. During the initial cure at 80 °C, a considerable amount of reactive cyanate groups remain in the network. After the drying and postcure treatment above the T_g of the cross-linked network, the cyanate doublet completely disappears. Thus, the drying allows for a simultaneous postcure.

The generation of the foam and full network formation were accomplished by subjecting the cyanurate networks to a thermal treatment in vacuum. The thermogravimetric analysis clearly shows that temperatures above the T_g of the cyanurate network (i.e., the T_g on the network cured to 80 °C) are required to facilitate solvent material (~120−160 °C). Foam formation and full network formation were accomplished by heating to 280 °C (8 h). Shown in Table 1 is the density after drying. A significant drop in density was observed for the dried samples which looked opaque and initially contained 16 wt % and higher contents of cyclohexane. Moreover, the density drop appears to be somewhat commensurate with the initial volume fraction of cyclohexane (i.e., the foam efficiency is high). However, the density begins to increase somewhat for the samples containing the higher volume functions of cyclohexane. This is believed to result from continuous or interconnected pores which take up the flotation fluid. Conversely, the samples which were observed to be homogeneous upon cure showed no detectable drop in density.

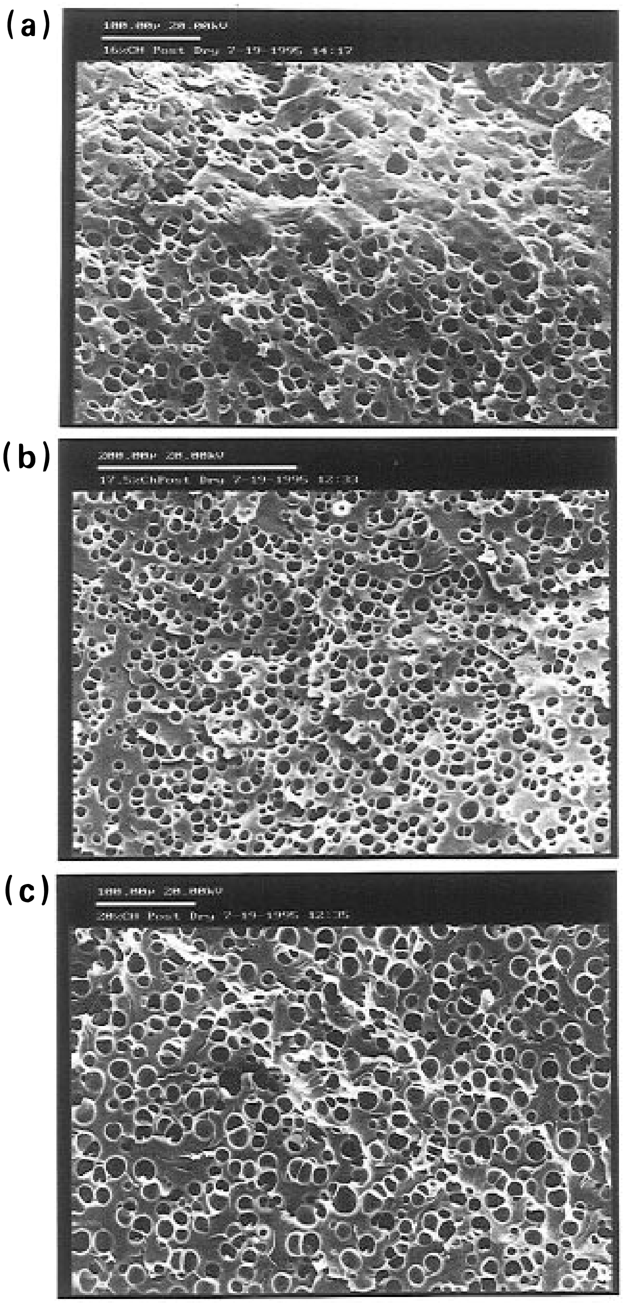

Figure 3. SEM micrographs of a dried cyanurate network which initially contained (a) 16, (b) 17.5, and (c) 20 wt % cyclohexane.

While the density column measurements showed that a foam structure had been achieved, no insight was

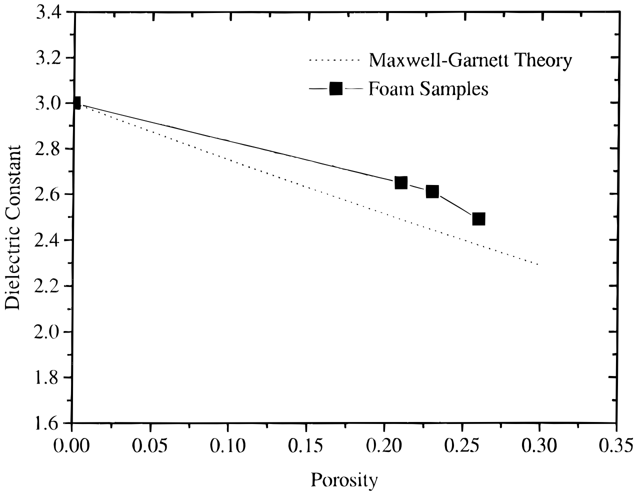

Figure 4. Dielectric constants at 1 MHz under a dry atmosphere at 20 °C versus porosity which is assumed to be the initial volume fraction of cyclohexane (—) and (···) predicted are plotted.

provided on the size of the pores. This issue was addressed with SEM. Figure 3 shows several SEM micrographs which initially contain 16, 17.5, and 20 wt % cyclohexane. From these micrographs, it is evident that a well-defined porous structure is obtained, with spherical pores having average diameters in the 10–20 μm range. Interconnectivity exists between the pores for those samples containing high volume functions of cyclohexane. The size scale of the phase separation is somewhat larger than that observed for both rubber and thermoplastic modified epoxides.

The dielectric constant of the pure cyanate resin under a dry (nitrogen) atmosphere at 20 °C is 3.0 (1 MHz).[20] For the microporous cyanate networks, the dielectric constant decreases with the porosity, as shown in Figure 4. In Figure 4, the solid and dotted lines represent experimental dielectric results together with the prediction of the dielectric constant from Maxwell-Garnett theory (MGT),[21] respectively. The experimental trend is in relatively good agreement with the simple theoretical estimates by MGT. The small discrepancies between experimental results and MGT prediction might be due to the error in estimated porosities. The porosities were calculated from the densities of the pore-forming solvent and the density of the matrix material, assuming that the entire amount of solvent was involved in the phase separation. Clearly, this is not the case, as evidenced by the miscibility of the lower contents of cyclohexane in the cyanate. Lower values of actual porosity would result in closer agreement of dielectric constants measured and predicted. Unfortunately, accurate measures of the porosity were not possible, as previously stated. Nonetheless, dielectric constant values as low as 2.5 were measured.

References and Notes

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MA960960Z