

Porous Epoxies by Reaction Induced Phase Separation with a Removable Alcohol Poragen

Joseph L. Lenhart^{1,2}, Robert J. Klein^{1,3}

¹US ARMY Research Laboratory, Aberdeen, MD 21005

²Sandia National Laboratories, Albuquerque, NM 87185

³Luna Innovations Incorporated, Charlottesville, VA 22903

INTRODUCTION

Porous organic and inorganic materials with both random and controlled microstructures have utility in a variety of fields including catalysis (1,2), sensors (1,2), separations (3), optical platforms (4), tissue engineering (5), hydrogen storage (6), micro-electronics, medical diagnostics, as well as other applications. A historical emphasis of porous polymers has been in separations technology (3) and many of these investigations have focused on a system composed of polystyrene crosslinked with divinylbenzene (7) in the presence of a poragen solvent. Some research has been conducted to bridge the gap from inorganic to organic materials through the use of hybrid type materials (8), which can be exploited to make porous structures. In addition, super critical CO₂ has shown utility in processing a wide range of porous materials including, metals, silica glasses, and polymers (9). Block copolymer techniques have proven successful at generating controlled morphology in polymers (10), and porosity can be generated in these structures by degradation and removal of one of the phases (11-12). However, the time scale required for obtaining these structures is long, which severely limits large scale applications. While the technique highlighted in this preprint is not likely to generate the complex series of microstructures observed in block copolymers, exploiting a polymer-solvent system to generate simple structures in a controlled manner, will enable the broader application of "templated" polymers.

This work highlights a simple mechanism for tuning the pore size in crosslinking systems by adding a solvent poragen that phase separates during the resin curing process (reaction induced phase separation, RIPS). The pore size was varied from ~ 100 nm to microns by simply controlling the resin reaction rate through the addition of an organic catalyst. Once the impact of polymer-poragen compatibility, as well as the relative rate of reaction kinetics to phase separation kinetics is understood, the technique should be generally applicable to a wide range of resin chemistries.

EXPERIMENTAL

All samples utilized the same di-functional epoxide mixed in stoichiometric proportions with a tetra-functional amine. The epoxide was glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) (BADGE), with average molecular weight 348 g/mol, obtained from Sigma-Aldrich. The amine was poly(oxypropylene)diamine (D230), a jeffamine, with average molecular weight 230 g/mol, obtained from Sigma-Aldrich. Structures of the BADGE and D230 are shown in Figure 1.

1-octadecanol (95 %) was obtained from Fisher Scientific. 1-methylimidazole (99+ %), under the trade name IMICURE AMI-1 curing agent, was obtained from Air Products and Chemicals. The densities of the epoxide, amine, and octadecanol are 1.160, 0.9702, and 0.8120 g/cm³, respectively, meaning that a sample designated 40 wt% octadecanol contains 48 vol%. This assumes additivity of volumes in the mixed state.

The epoxide and amine were mixed in stoichiometric proportions with a mechanical mixer for 5 min at 1500 rpm. The octadecanol was melted in an 80-90 °C oven in predetermined masses, the epoxy liquid was pre-heated to 90 °C, and the two liquids were mixed at ~90 °C for 2 min at 1200 rpm. The octadecanol, which crystallizes at about 58 °C, was processed above 70 °C at all times. If needed, methylimidazole was measured (via a micro-pipette) and added immediately prior to the final mixing stage. Samples were cured for 15 h at the specified

temperatures. They were then fractured at 0 °C, and the octadecanol was removed under a 125 °C vacuum for 17 h.

Images were taken with a Zeiss Supra55VP, field emission gun, scanning electron microscope. Samples were coated with a gold-palladium mixture and imaged with 5 kV accelerating voltage, in high vacuum mode. For most samples a secondary electron detector was used (working distance 15 mm), but in surfaces where pores were very small or not present (pore diameter < 50 nm), a shorter working distance (5 mm) and the in-lens detector were used.

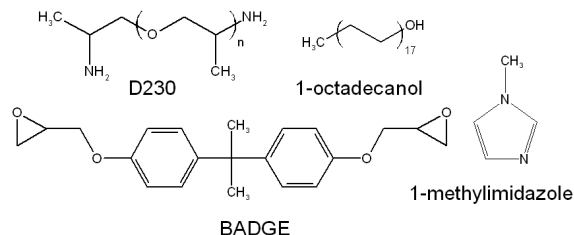


Figure 1. Structures of the BADGE (epoxide), D230 (amine crosslinker), 1-octadecanol (poragen), and 1-methylimidazole (catalyst).

RESULTS

Composition plays a critical role in phase separation of this system. As composition increases from 30 wt% to 50 wt% octadecanol at a cure temperature of 90 °C, the pores in Figure 2 increase from barely visible with the SEM (diameters on the order of 10 nm) to extremely large (~3 microns). To the naked eye, the 30 wt% sample is optically transparent whereas samples with higher octadecanol fraction are opaque and appear white.

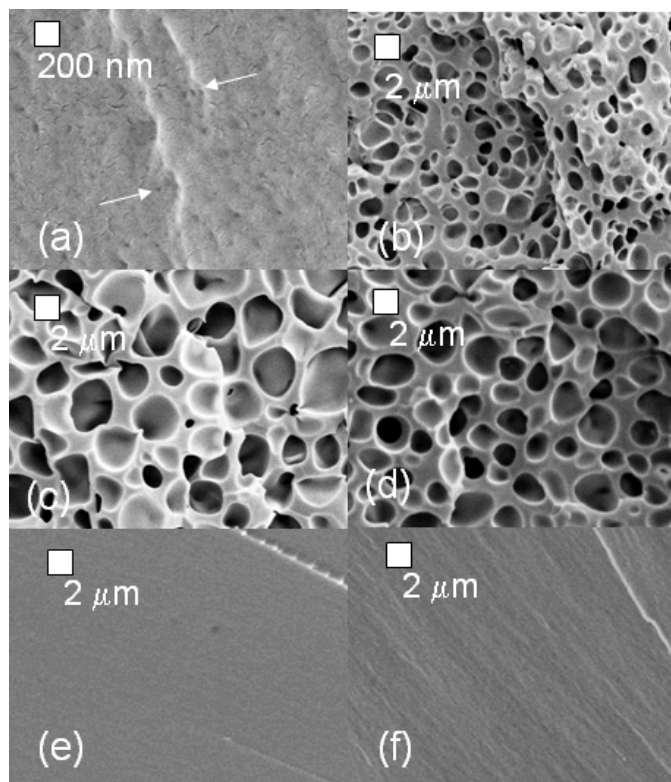


Figure 2. Epoxies cured at 90 °C, where the octadecanol has been evaporated, for (a) 30 wt% octadecanol; (b) 40 wt% octadecanol; and (c) 50 wt% octadecanol. (d) epoxy cured at 75 °C with 40 wt% octadecanol. Arrows indicate the location of small pores. Images (e) and (f) indicate 40 wt% octadecanol loaded epoxies cured at 90 and 75 °C respectively, prior to evaporation of the octadecanol.

Cure temperature is also an important variable, and delineates in rough terms the impact of cure rate. As cure temperature decreases from 90 to 75 °C (micrograph (d) versus (b) in Figure 2), pore diameter increases by a factor of ~2. In terms of the primary driving force impacting the pore size as the temperature is lowered, it is difficult to distinguish between thermodynamic miscibility between components and the kinetic-based time to gel. However, based on the qualitative observation that the sample at 75 °C takes significantly longer to gel than a sample at 90 °C, as well as the more spheroidal pore shapes in the 75 °C micrograph, we hypothesize that the reaction kinetics and the resulting time to gel is the predominant factor. As temperature decreases, reaction rate decreases, time to gel increases, and the components have longer times to phase separate.

If this hypothesis is true, the addition of a catalyst to increase the reaction kinetics will decrease the average pore size. The addition of small fractions of methylimidazole can increase the resin cure rate substantially. The imidazole was systematically used to "quench" pores at early stages of growth, prior to extensive growth of octadecanol inclusions. The fraction of imidazole is sufficiently small in the mixtures here that it will not lead to significant shifts in composition on a thermodynamic phase diagram, so changes observed in morphology must arise from kinetically arresting the process of phase separation. Figure 3 illustrates the decrease in pore size with increasing catalyst as the approximate pore diameter changes from ~ 2 microns to 200 nm as the catalyst loading increases from 0 to 0.5 wt%. The pore size is fairly sensitive to reaction rate, as the gel time for 40% octadecanol loaded resins with 0, 0.3, and 0.5 wt% methylimidazole is approximately 33, 28, and 25 min, respectively.

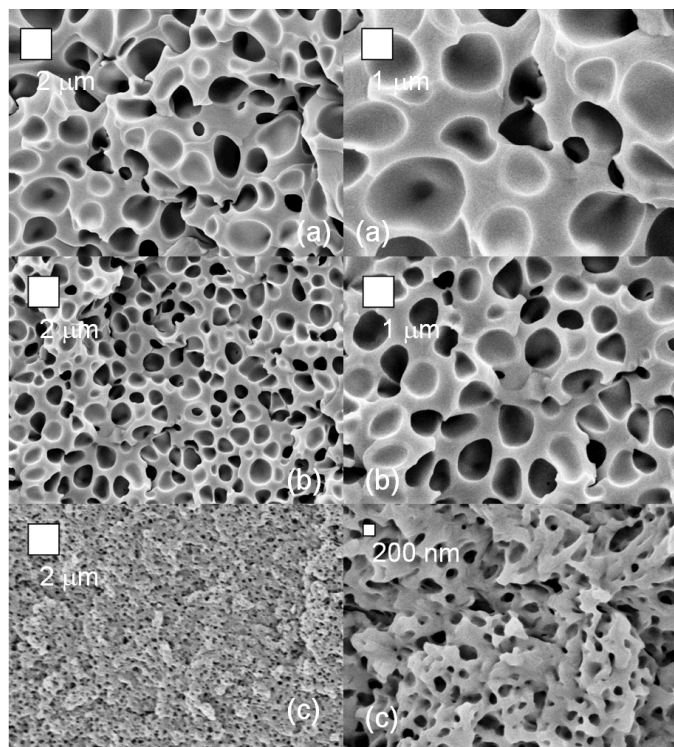


Figure 3. Fracture surfaces of epoxies cured at 90 °C with 40 wt% solvent: (a) 0.3 wt% catalyst; (b) 0.4 wt% catalyst; and (c) 0.5 wt% catalyst.

SUMMARY

This paper demonstrates RIPS, a simple and broadly applicable method to control pore size over an order of magnitude, from the micron to the 100 nanometer scale. For this resin system, the sacrificial phase, octadecanol, is removed by vacuum-assisted evaporation once the epoxy components have reacted to form a solid,

porous matrix. The pore diameter is controlled through variations in cure temperature and the addition of the catalyst methylimidazole, both of which effectively varies the resin reaction rate. Future work will focus on investigating the limitations of this process as well as controlling the pore connectivity and shape with the application of external fields. In addition, sub-micron and nano-particulates will be incorporated into the porous materials to enable additional control over the mechanical, electrical, thermal, and mass transport properties.

ACKNOWLEDGEMENTS

This work was initiated at Sandia National Laboratories by J.L. Lenhart and R.J. Klein and is being continued at the US Army Research Laboratory by J.L. Lenhart. Address correspondence to J.L. Lenhart; 410-306-1940; joseph.lenhart1@arl.army.mil. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendations by the Army Research Laboratory nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

REFERENCES

1. C. J. Brinker, G. W. Scherer, "Sol Gel Science: The Physics and Chemistry of Sol-Gel Processing," Academic Press, Inc, New York, NY (1990).
2. M. E. Davis, *Nature*, **417**, 813 (2002).
3. F. Svec, C. G. Huber, *Anal. Chem.*, 2101, April (2006).
4. B.J. Scott, G. Wernsberger, G.D. Stucky, *Chem. Mater.*, **13**, 3140 (2001).
5. S.J. Hollister, *Nature Materials*, **4**, 518 (2005).
6. J. Germain, J. Hradil, J.M.J. Frechet, F. Svec, *Chem. Mater.* **18**, 4430 (2006).
7. F. Svec, J.M.J. Frechet, *Science*, **273**, 205 (1996).
8. K.J. Shea, D.A. Loy, *Chem. Mater.*, **13**, 3306 (2001).
9. A.I. Cooper, *Adv. Mater.*, **15**, 1049 (2003).
10. F.S. Bates, G.H. Fredrickson, *Physics Today*, **52**, 32 (1999).
11. Li, S.; Garreau, H.; Vert, M.; Petrova, T.; Manolova, N.; Rashkov, I., *J. Appl. Polym. Sci.* **1998**, *68*, 989.
12. Durke, D.A.; Gomez E.D.; Ellsworth M.W.; Bell A.T.; Balsara, N.P. *Macromolecules*, **2007**, *40*, 5103.