

Removable Foams Based on an Epoxy Resin Incorporating Reversible Diels–Alder Adducts

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ABSTRACT: We have successfully incorporated Diels–Alder reversible chemistry into epoxy resins. The Diels–Alder chemistry goes in the forward direction at 60 °C and reverses at or above 90 °C. One resin was formulated with other commercial ingredients into foamed epoxy. The foam, shown to have mechanical properties similar to foams formed with conventional epoxy resins, is being utilized for electronic encapsulation. Because of the built-in reversible chemistry, the foams can be easily removed by dissolution in 1-butanol at 90 °C. Removal allows for the rework, upgrading, or dismantlement of the electronic components. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1496–1502, 2002

Key words: Diels–Alder polymers; resins; blowing agents

INTRODUCTION

Foamed polymeric encapsulants are used to protect high-value electronic and electromechanical components from shock and vibration and provide thermal insulation. The most common encapsulants are rigid, thermosetting polyurethanes and epoxies. The typical process is to enclose the electronics in a mold and then pour the premixed reactive components into the mold. The reactants simultaneously foam and cure around the electronics, and then the mold is removed. For some electronic components, it is important to be able to remove the encapsulant at a later time for repairs, upgrades, or salvage of expensive components (Figure 1). These needs require an encapsulant that can be easily removed without damage to components or sacrificing the good mechanical properties of an epoxy or polyurethane. We are developing new encapsulants for this purpose that have mechanical properties that are similar

to conventional encapsulants, but can be removed under controlled external stimuli. Conventional encapsulants (epoxies and polyurethanes) are difficult to remove because of their crosslinking, solvent resistance, and mechanical toughness. In some instances, these materials have been removed by resorting to harsh means, such as chiseling, or by using very aggressive solvents, such as *n*-methyl pyrrolidinone.

Our approach to a removable polymeric foam encapsulant is to introduce chemically labile linkages within crosslinked polymeric networks. We have explored the [4 + 2] cycloaddition reaction between dienes and dienophiles known as the Diels–Alder reaction.^{1–3} Specifically, we were interested in the thermally reversible reaction between appropriately functionalized furan and maleimide monomers. It is well established that Diels–Alder adduct formation between furans and maleimides is favored at mild temperatures between room temperature and 60 °C.^{4,5} During this process, two isomers, endo and exo, are formed, with the latter isomer being thermodynamically more stable. The reverse (retro) Diels–

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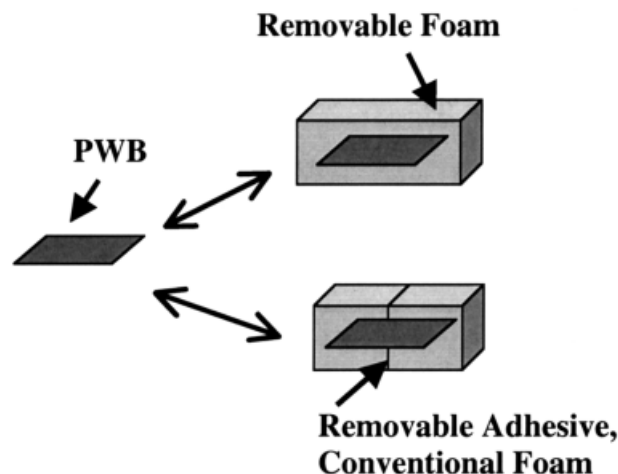


Figure 1 Possible ways to remove an encapsulated PWB.

Alder reaction is favored by heating to temperatures of ≥ 90 °C (Figure 2).

We incorporate furan-maleimide Diels–Alder adducts into epoxy-based resins and use them in well-established curing reactions with amines to prepare removable encapsulants. The reaction between oxirane (epoxide) groups and amines leads to highly crosslinked materials. This epoxy is prepared as a two-part liquid system that allows for easy processing. One part consists of epoxy resins, whereas the second part contains primary or secondary amine curing agents. The two components are mixed at room temperature just prior to use. Chemical crosslinking occurs during the reaction forming an insoluble crosslinked epoxy thermoset. The thermally reversible Diels–Alder linkages within these crosslinked epoxy networks allow for their easy removal.

EXPERIMENTAL

Materials

Reagent grade reactants and solvents were obtained from Aldrich Chemical Company, Inc. (4-

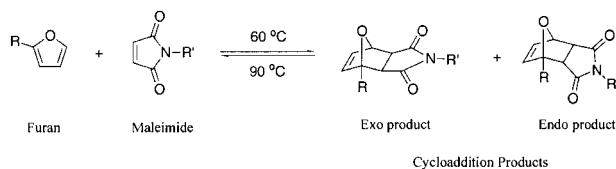


Figure 2 Reversible Diels–Alder reaction between furan and maleimide.

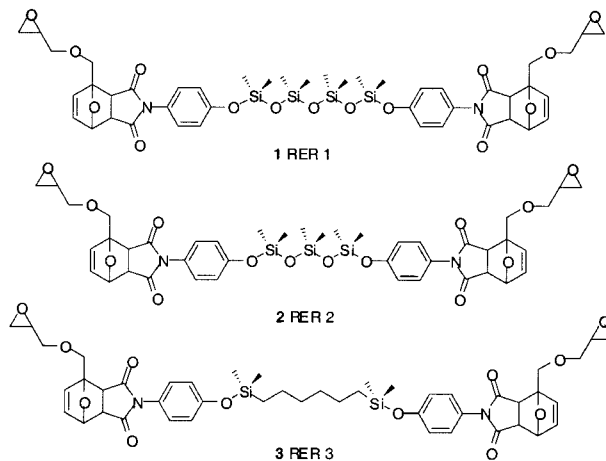
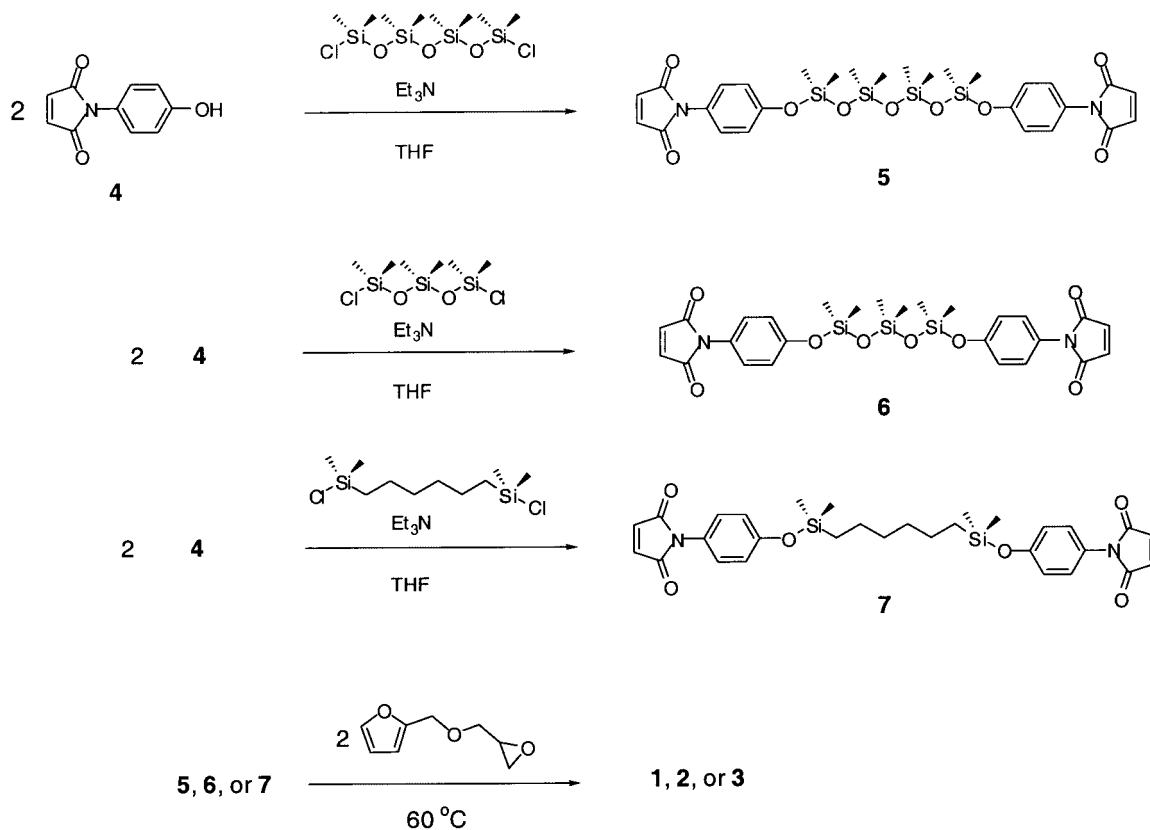


Figure 3 Thermally reversible Diels–Alder epoxy resins 1–3.

aminophenol, maleic anhydride, furfuryl glycidyl ether, furfuryl amine), Fisher Scientific (acetone, *N,N*-dimethyl formamide [DMF], 2-propanol, diethyl ether, tetrahydrofuran, phosphorous pentoxide, triethylamine [Et₃N], sulfuric acid, anhydrous magnesium sulfate [MgSO₄]), or Gelest, Inc. (1,7-dichlorooctamethyltetrasiloxane, 1,5-dichlorohexamethyltrisiloxane, 1,6-bis(chlorodimethylsilyl)-hexane). Epoxy resins and curatives were obtained from Shell Chemical Company (Shell EPON 8121, Shell Epi-Cure 3270), and Air Products, Inc. (Ancamine 2049 [3,3'-dimethylmethylene-(cyclohexylamine)]). The silicone surfactant was obtained from Air Products, Inc. (DABCO® DC193). The foam blowing agent was obtained from 3M™ (fluorinert FC-72 electronic fluid). All materials were used as received.

Resin Synthesis

Bis-epoxy resins (1–3) were prepared and are shown in Figure 3. Resin preparation was achieved in four synthetic steps from commercial materials. We required resins that contained appropriately functionalized furans and maleimides. We chose 4-hydroxyphenyl maleimide 4 as our dienophile for resins 1–3 because it contains a reactive phenolic group to which a tether may be attached allowing for tuning of resin properties. Furfuryl glycidyl ether was chosen as the reactive diene for all resins shown. The selection of furfuryl glycidyl ether as the furan introduces epoxide functionality in the final step of resin synthesis. Similarly, curatives have been prepared by utilizing furfuryl amine in place of furfuryl glycidyl



ether in the final synthetic step. 4-Hydroxyphenyl maleimide is prepared according to the literature.⁶

Removable Diels–Alder resins, 1–3, are each prepared in an analogous manner. Bis-maleimide precursors, 5, 6, and 7 are prepared by reacting 2 equivalents of 4-hydroxyphenyl maleimide 4 with one equivalent of 1,7-dichloroocta-methyltetrasiloxane, 1,5-dichlorohexamethyltrisiloxane, or 1,6-bis(chlorodimethylsilyl)-hexane, respectively, in $\text{Et}_3\text{N}/\text{THF}$ solution for 4 h at ambient temperature (Scheme 1). The reaction is filtered to remove hydrochloride salts and concentrated *in vacuo*. The resulting oil is dissolved in diethyl ether, washed with water, dried (MgSO_4), and concentrated to yield bis-maleimides 5, 6, and 7 as low melting yellow solids or amber oils in ~95% yields: compound 1, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.15 (d, $J = 8.8$ Hz, 4H), 6.95 (d, $J = 8.8$ Hz, 4H), 6.80 (s, 4H), 0.23 (s, 12H), 0.082 (s, 12H); compound 2 $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.14 (d, $J = 8.8$ Hz, 4H), 6.94 (d, $J = 8.8$ Hz, 4H), 6.80 (s, 4H), 0.23 (s, 12H), 0.082 (s, 6H); compound 3, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.14 (d, $J = 9.2$ Hz, 4H),

6.87 (d, $J = 9.2$ Hz, 4H), 6.79 (s, 4H), 1.38–1.29 (m, 8H), 0.74–0.70 (m, 4H), 0.23 (s, 12 H).

Resins 1–3 are prepared by heating bis-maleimides 5, 6, or 7 to 60 °C until they flow as low viscosity oils. Two equivalents of furfuryl glycidyl ether are then added, and the materials are intimately mixed for 1 h at room temperature. The mixture is placed in an oil bath, stirred, and heated at 60 °C for 24 h. Resulting resins 1–3 are high-viscosity, amber oils at room temperature and are used without further purification. Upon heating to 60 °C, the resins become lower-viscosity materials, allowing for easier processing.

Removable, Physically Blown Epoxy Foams

A formulation used for making removable epoxy foams at a density of 0.15 gm/cm^3 and using the removable epoxy resin (RER 1), containing reversible Diels–Alder linkages, is shown in Table I. The formulation is based on a method similar to one in which only commercial ingredients are used and that produces a nonremovable foam.⁷ The formulation was packaged as a two-part kit.

Table I Removable Blown Epoxy Foam Formulation, REF100

Ingredient	Amount
Part A	
Removable Epoxy Resin (RER 1)	60% of resin
Shell EPON 8121 epoxy resin	40% of resin
Part B	
Air Products Ancamine 2049 curative	31 phr ^a
Shell Epi-Cure 3270 curative	12 phr
Air Products DC-193 surfactant	9 phr
3M Fluorinert FC-72 blowing agent	25 phr

^a phr, parts/hundred resin.

Part A contained the two resins and Part B contained all of the remaining ingredients. The two resins in Part A mix readily and stay mixed indefinitely. The curatives in Part B are totally miscible, but the FC-72 blowing agent does not dissolve or disperse well in the curing agent mixture. Thus, the surfactant is added not only as a foam stabilizer, but also as a dispersant for the FC-72 in the curatives. When the ingredients in Part B are vigorously shaken for several minutes, the blowing agent disperses uniformly and remains in dispersion for up to 1 h.

After both Part A and Part B are fully blended, appropriate amounts (i.e., 56.5% Part A, 43.5% Part B) are added together and mixed thoroughly by spatula or mechanical mixer for ~1 min. The mixture is poured or injected into a metallic mold. Mold release allows for extraction of the encapsulated parts. The mold is placed in a forced convection oven at 65 °C for 4 h. A post-cure at 75 °C is performed to elevate the glass transition temperature, T_g . After cure, the mold is cooled to room temperature and the foam removed.

Scanning Electron Microscopy

Scanning Electron microscopy (SEM) was performed on a JOEL JSM-6400XV scanning electron microscope. Foam samples were sputter coated with gold/palladium prior to SEM analysis. Samples were photographed at 30× and 100× magnifications.

Mechanical Property Measurements

Compressive and tensile strengths and moduli were acquired for removable epoxy foams of approximate density 0.13 gm/cm³ using an Instron Series IX Automated Materials Testing System

(Instron Corp., Canton, MA). Cylindrical foam samples were 2.54 cm long and 2.87 cm diameter (i.e., 6.45 cm² [1 in²] cross-sectional area). Tests were run at room temperature with a 454-kg load cell and a crosshead speed of 0.127 cm/min. Dynamic mechanical analysis (DMA) data were collected using a Rheometrics ARES Dynamic Spectrometer (Rheometrics Corp., Piscataway, NJ). The dynamic testing was rectangular torsion on 5.08 cm long × 1.27 cm wide × 0.63 cm thick samples over a temperature range 30–150 °C at a rate of 2 °C/min. The torsional frequency was 1 Hz.

RESULTS AND DISCUSSION

We required resins that could be easily prepared in high yield and allowed for versatile processing. Ideally, we wanted resins that were low viscosity liquids or oils and that could be easily dissolved or mixed with liquid amine curing agents and other additives. We found that the use of siloxane tethers between Diels–Alder adducts in resins 1–3 provided materials that were low viscosity oils at elevated temperatures (60 °C). Resins 1 and 2 are designated Removable Epoxy Resin (RER) 1 and 2, respectively. RER 1 contains a tetrasiloxane tether between Diels–Alder adducts, whereas RER 2 contains a trisiloxane tether. Resin 3 (RER 3) contains a bridged bis-siloxane hexyl tether between Diels–Alder adducts. We have utilized RER 1 in the preparation of removable blown epoxy foams.

In addition to resins and curing agents, an epoxy foam is prepared with a blowing agent and a surfactant.⁸ For a blowing agent, we have selected Fluorinert FC-72 electronic fluid, which has a boiling point of 56 °C. This boiling point is convenient for curing the epoxy foam at 65 °C, a typical epoxy cure temperature. Surfactants are used to promote foaming and stabilization of the subsequent cellular structure. The surfactants used in polyurethane foam systems, such as silicone-based surfactants, are generally the same ones used in epoxy foams. Benning⁹ notes that cell structure can be greatly affected by the surfactant, which in turn influences the properties of the resultant foam. We have selected Air Products DABCO® DC193, which is a silicone surfactant.

There are several important criteria in developing a desirable foam structure. First, the rheology of the epoxy mixture during the rise of the

foam is very important. As the epoxy and curing agent cross-link and cure, viscosity increases. The viscosity increase is necessary to retain the cell structure created during the rise of the foam. An epoxy that does not become sufficiently viscous to maintain a cellular structure during rising of the foam will coalesce and collapse. An epoxy that becomes viscous too early during the cure may terminate the foam rise, not allowing for full expansion. A second important processing parameter closely related to foam rheology is the epoxy cure rate, which is largely dependent on the processing temperature. A very fast reacting epoxy-curable system with a large exotherm may result in a cure rate that does not allow sufficient processing time for the foam to rise. Furthermore, an excessive amount of heat from a large exotherm could result in burn out of the interior regions of the foam. Conversely, an extremely slow reacting epoxy may not become viscous and gel within an appropriate amount of time to establish a cellular structure during the foam rise, requiring addition of external heat or a reaction accelerator to increase the cure rate. Another processing parameter that affects epoxy foam cell structure is surface tension. Surfactant is added at an appropriate level to control the surface tension of the fluid.

A dual resin/dual curative system used in the REF100 foam formulation was chosen because it provides the capability to tailor the reactivity of the foam system for a given application. The resins were selected such that there is a lower reactivity resin (RER 1) and a more highly reactive resin (EPON 8121) so that the resin ratio can be modified to adjust the reactivity of the foam system. Likewise, a more highly reactive curing agent (Epi-cure 3270) and a curing agent with lower reactivity (Ancamine 2049) were chosen so that the curative ratio could be adjusted to control

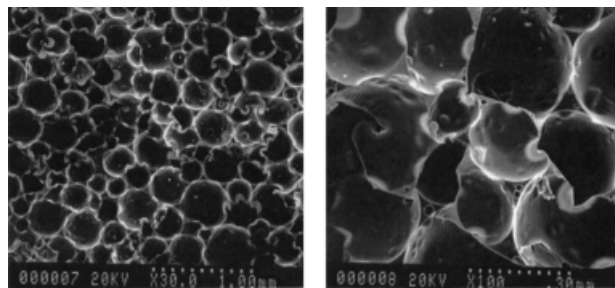


Figure 4 Scanning electron microscopy (SEM) photographs of REF100 removable epoxy foam microstructure: 30 \times magnification (left), 100 \times magnification (right).

Table II REF100 Compressive Strength and Modulus

Density (g/cc)	Young's Modulus (MPa)	Max. Compressive Strength (MPa)
0.123	23.1	0.70
0.130	26.9	0.79
0.131	28.4	0.77
0.138	30.9	0.78
0.138	34.2	0.82
Mean: 0.131	28.7	0.77

system reactivity and exotherm. The ability to tailor system reactivity and exotherm using resin and curative ratios provides a method to modify the foam system for larger volumes and other densities. Larger foam volumes produce higher exotherm temperatures because the foam is a self-insulating material that does not allow internal heat to be readily conducted out of the material. It is possible that with larger samples the exotherm could be sufficiently high to prematurely cure the epoxy such that full expansion is not achieved. Furthermore, it is possible that the exotherm in larger samples could be high enough to burn out the interior of the foam. In such cases, the resin and/or curative ratios could be adjusted to lower the exotherm and avoid foam processing problems.

The SEM spectra of the REF100 removable epoxy foam microstructure are shown in Figure 4. The morphology of this foam is virtually identical to that of a nonremovable epoxy foam made with only commercial ingredients.⁷ It is a closed-celled structure with fairly spherical shaped cells. Nominal cell size for foams of 0.16 to 0.32 gm/cm³ density is \sim 300 μ m. Cell sizes for lower density foams tend to be marginally larger than for higher density foams.

Compressive strengths and moduli for five foam samples in the density range 0.12–0.14 gm/cm³ are shown in Table II. Tensile strengths and moduli for five foam samples in the density range 0.13–0.14 gm/cm³ are shown in Table III. The mean compressive and tensile moduli were 28.7 and 35.6 MPa, respectively. A comparison of the mean maximum compressive strength and the ultimate tensile strengths of the samples indicate that the removable epoxy foam is stronger in compression than in tension. This behavior is consistent with compressive and tensile data collected for the conventional epoxy foam EF-AR10/20, for

Table III Tensile Strength and Modulus of Removable Epoxy Foams

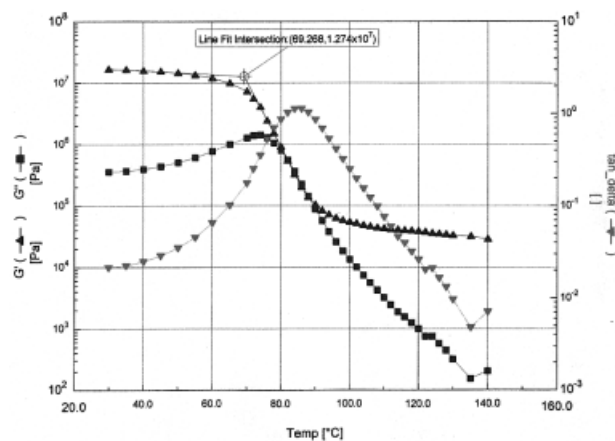
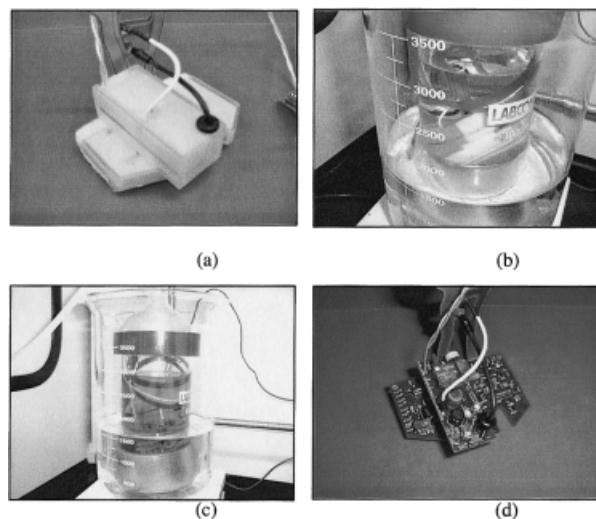
Density (g/cc)	Young's Modulus (Pa)	Ultimate Tensile Strength (Pa)
0.128	33.5	0.46
0.131	35.0	0.46
0.133	33.8	0.43
0.135	36.9	0.39
0.139	39.0	0.43
Mean: 0.133	35.6	0.43

which maximum compressive strength was also greater than ultimate tensile strength.⁷

Shear and loss moduli versus temperature (DMA) results for a sample of removable epoxy foam of density 0.14 gm/cm³ are shown in Figure 5. The shear modulus in the glassy region of the curve is ~20.0 MPa. The T_g derived from the shear modulus plot is 69 °C. (Alternatively, the T_g based on the maximum in tan delta is 85 °C.)

Compressive and tensile strengths and moduli were ~40% lower than those of conventional epoxy foam of the same density.⁷ This result may be because the RER 1 resin used in the removable foam has a higher molecular weight than the resins used in the conventional foam. The longer, more flexible molecular bridge between crosslinked epoxy functional groups may result in a lower modulus and a lower T_g for the removable foam. For any foam, modulus is highly dependent on foam density.

When there is a sufficient amount of removable resin combined with conventional epoxy resin,

**Figure 5** Dynamic mechanical analysis (DMA) of removable epoxy foam at a density of 0.14 g/cm³.**Figure 6** Removal of REF100 removable epoxy foam: low voltage electronic assembly (a) before foam removal, (b) at the start of the removal process in *n*-butanol at 90 °C, and (c) at the end of the removal process; (d) low voltage module after foam removal.

and the foam is immersed in a mild solvent such as 1-butanol at 90 °C, the Diels–Alder functionalities reverse, and the crosslinked epoxy structure dissolves. The corresponding nonremovable foam of the same density would be unaffected by 90 °C 1-butanol. Foam removal experiments have demonstrated that the REF100 foam is removed completely from components using this dissolution technique. The process of removing REF100 removable foam from a low voltage electronic assembly is demonstrated in Figure 6.

CONCLUSIONS

Removable foam encapsulants allow for repair, upgrading, and dismantlement of electronic components. Removable bis-epoxy resins have been prepared in four synthetic steps from commercial materials. The removability is based on the thermally reversible Diels–Alder reaction between substituted furans and maleimides that is incorporated within the epoxy resin. With one resin, RER 1, we have formulated a physically blown epoxy foam. The foam has mechanical properties that compare with epoxy foams made with commercial resins. In addition, the foam can be dissolved under mild conditions using 1-butanol at 90 °C. The removability allows one to use the

foam as an encapsulant for electronic components and then remove the encapsulant when desired.

Such removable epoxies may have a number of additional uses in encapsulation and adhesion where mild removal conditions are allowed. We are currently investigating additional resins incorporating the Diels–Alder functionality for numerous applications, including adhesives, coatings, and structural composites.

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REFERENCES

1. Aubert, J. H.; McElhanon, J. R.; Saunders, R. S.; Sawyer, P. S.; Wheeler, D. R.; Russick, E. M.; Rand, P. B.; Loy, D. A. *Progress in Developing Removable Foams, Adhesives, and Conformal Coatings for the Encapsulation of Weapon Components*; Sandia Report, Sandia National Laboratories, SAND 2001-0295, February 2001.
2. Loy, D. A.; Wheeler, D. R.; Russick, E. M.; McElhanon, J. R.; Saunders, R. S. Method of making thermally removable epoxies. U.S. Patent 6,337,384, January 8, 2002.
3. Small, J.; Loy, D. A.; Wheeler, D. R.; McElhanon, J. R.; Saunders, R. S. Method of Making Thermally Removable Polymeric Encapsulants. U.S. Patent 6,271,335, August 7, 2001.
4. Chugo, Y.; Sada, K.; Saegusa, T. *Macromolecules* 1990, 23, 2636.
5. Canary, S. A.; Stevens, M. P. *J Polym Sci Part A: Polym Chem* 1992, 30, 1755.
6. Park, J. O.; Jang, S. H. *J Polym Sci Part A: Polym Chem* 1992, 30, 723.
7. Russick, E. M.; Rand, P. B. Development and Characterization of a New Epoxy Foam Encapsulant as an Ablefoam Replacement, Sandia Report, Sandia National Laboratories, SAND98-2538 (December 1998).
8. Frisch, K. C.; Saunders, J. H. *Plastic Foams, Part II*; Marcell Dekker: New York, 1973.
9. Benning, C. J. *Plastic Foams: The Physics and Chemistry of Product Performance and Process Technology*; Wiley-Interscience: New York, 1969.