

Nanostructured Multifunctional Materials by Cure-Driven Phase Separation

FINAL REPORT

CONTRACT NO. N00014-00-C-0443

Covering Period January 8, 2001 to January 7, 2002

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October 2003

20031017 144

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE

October 2003

3. REPORT TYPE AND DATES COVERED

Final Report 08Jan01 – 07Jan02

4. TITLE AND SUBTITLE

Nanostructured Multifunctional Materials by Cure-Driven Phase Separation

5. FUNDING NUMBERS

C – N00014-00-C-0443

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

EIC Laboratories, Inc.
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REPORT NUMBER

200002F

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

DARPA/DSO
3701 North Fairfax Drive
Arlington, VA 22203-171410. SPONSORING/MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

An investigation was conducted into the development of a self-healing fiber reinforced polymer (FRP) composite based on a nanostructured epoxy matrix resin, recently developed by EIC Laboratories. This novel material comprises a blend of epoxy and amphiphilic block copolymer, which separates during cure to form three separate phases of high strength epoxy, rubbery polar polymer and rubbery nonpolar polymer. The high strength epoxy and polar rubbery polymer are arranged in cocontinuous networks, while the third nonpolar rubbery polymer is arranged as discrete domains evenly distributed throughout the material. Reactive monomers, added to the uncured mixtures, will segregate into one of the rubbery phases depending on compatibility and will be free to diffuse to and repair, by polymerization, any voids formed in the matrix through microcracking or other accumulated damage. Segregated from the epoxy phase, these monomers do not plasticize or otherwise compromise the thermal mechanical properties of the matrix system. This study verifies the structure of the EIC material and provides evidence for the incorporation of active monomers within this material. The effect of these monomers on the durability and mechanical properties of composites is also assessed.

14. SUBJECT TERMS

Composite, Self-healing, Nanostructured, Epoxy, Block copolymer, Blend

15. NUMBER OF PAGES

20

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION
OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION
OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

SAR

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EXECUTIVE SUMMARY

An investigation into the development of a self-healing composite was conducted. The self-healing composite utilizes a multiphase nanostructured epoxy as a matrix material. This epoxy comprises three phases distributed throughout the material, including cocontinuous domains of high strength epoxy and ionically conductive poly(ethylene glycol) (PEG). A third phase, comprising poly(dimethyl siloxane) (PDMS), is distributed throughout the material in discrete nanosized domains. Self-healing functionality is imparted to this system by incorporating reactive monomers within the PEG or PDMS domains. Within these domains, the monomers are stabilized against polymerization. The monomers are free to diffuse throughout the material and accumulate in voids formed by microcracks or other mechanical damage. These are then free to polymerize and repair the void.

This report provides a summary account of the investigation of this system. An introduction provides an overview of the approach including specific objectives and research team participants. A technical background section (page 2) provides a description of the nanostructured epoxy developed by EIC Laboratories and its use as a reservoir and conduit for the transport of organic liquids. The technical progress section (page 5) is divided into four subsections. These include: a characterization of the nanostructured epoxy including a TEM micrograph of the structure, along with an account of the development of a high temperature version of the epoxy suitable for use in temperatures exceeding 150°C. The investigation of monomer systems used as self-healing agents is provided on page 9. This subsection describes the method of monomer incorporation in the epoxy mixtures and the confirmation of monomer survival within the cured epoxy. A third subsection (page 12) provides an account of preliminary attempts to discern self-healing in suitably modified nanostructured epoxies through the use of mechanical testing. A final subsection (page 14) describes more recent work on the exploitation of the electrochemical properties of the resin. These have the potential of providing composites with inherent sensing capabilities. They also provide a different approach toward the development of a self-healing matrix via *in situ* electrochemical polymerization of entrained monomers. A summary of the results and conclusions are provided on page 15.

1.0 INTRODUCTION

Thermosetting epoxy resins are the predominant matrix materials used in high performance fiber reinforced polymer composites. Recently, a novel multiphase, nanostructured epoxy resin was developed by EIC Laboratories, Inc. This epoxy incorporates a block copolymer surfactant, which structures the epoxy by undergoing sequential phase separation during cure. It was believed that this process led to the formation of interpenetrating networks of high-strength, glassy epoxy and viscous, ionically conductive, liquid-like polymer. It was further believed that these cocontinuous networks are nanoscale in size. The macroscopic material exhibits the high modulus and high glass transition temperature (T_g) characteristic of an engineering grade epoxy, combined with several unique and potentially valuable features. These include a moderate level of ionic conductivity and the ability to sequester sizable amounts of organic liquids without adversely affecting the thermal and mechanical properties of the material. It is believed that these several unique features offer the potential to provide multiple functionality to fiber-reinforced composites employing EIC's novel epoxy as a matrix material.

A study was undertaken to determine the feasibility of fabricating multifunctional composites using the epoxy and to further explore the morphology and governing parameters of this novel material. In addition to use as structural materials, proposed functionalities included biological and chemical self-decontamination. These functionalities would derive from the diffusion of ions (Ag^+) or decontaminating reagents from within the matrix material to the surface of the composite. Alternatively, the materials might be engineered to provide rapid permeation of chemical warfare agents into the matrix and subsequent decontamination in nanodomain "reactors". The development of remote sensing functionality was also proposed. This would take advantage of the matrix materials ionic conductivity to support the redox switching of various redox active moieties and deriving diagnostic analyses from the redox response. However, early consultation with DARPA revealed an eagerness to pursue self-healing capabilities and this was the primary focus of the research effort.

Composite self-healing has been an ongoing objective of a considerable number of research efforts (1,2,3). Fiber reinforced polymer matrix composites respond to mechanical insults, such as impacts or overextensions, through a process of microcrack formation. This permits the composite to absorb an enormous amount of mechanical energy without experiencing failure. However, over time as microcracks coalesce to form larger voids, this accumulated damage can become more severe, eventually leading to interply delamination and finally catastrophic failures, such as compressive buckling. Composite structures are often overbuilt to compensate for this process. If the composite could be repaired while the damage was still in the microcrack stage, it would be possible to greatly extend the service life of composite structures, while simultaneously reducing the size and weight of the materials used.

In an organic matrix, microcrack formation generally involves the rupture of covalent bonds. In most cases, these ruptures cannot be healed by annealing or through some other physical process. Additionally, the cracks though microscopic still comprise a substantial void that can only be filled by a liquid. Most self-healing strategies employ a liquid repair agent, which diffuses into the crack from a local reservoir and upon polymerizing heals the crack by in effect "gluing" together the sides of the crack. In the proposed effort, this self-healing monomer is sequestered throughout the macroscopic material within the nanosized domains of the phase-separated epoxy.

This liquid healing agent would freely diffuse through the material and accumulate within any void. Polymerization would be induced by chemical differences between the environment within the void and that experienced by the entrained monomer. The nature of these differences is discussed below in the technical background section of this document.

The overall goal of the proposed research effort was the fabrication of an epoxy matrix composite possessing a self-healing capability. Specific objectives included:

1. characterization and confirmation of the proposed morphology of the nanostructured epoxy resin,
2. sequestering of reactive monomers in a cured self-structured epoxy resin,
3. accumulation and polymerization of sequestered monomers in a microscopic void,
4. fabrication and characterization of fiber reinforced composite specimens using the nanostructured epoxy and formulation modified for self-healing capabilities,
5. verification of self-healing in a composite by mechanical analyses.

A research team assembled for this purpose included Drs. Michael D. Gilbert and Stuart Cogan of EIC Laboratories, Inc., with responsibility for development of the self-healing monomer systems, synthesis and formulation of matrix materials and overall management of the research effort. Professor John K. Vander Sande of MIT provided characterization of the matrix material morphology using primarily transmission electron microscopy (TEM). Robert Koon, of the Technology Development and Integration, Airframe Design at Lockheed Martin Aeronautics Company (LMAC), provided composite specimen fabrication and testing. Professor Mark Spearing of MIT provided additional composite fabrication and testing.

2.0 TECHNICAL BACKGROUND

Nanostructured epoxies were developed at EIC Laboratories, Inc. under an Air Force funded SBIR contract, for use as electrically releasing high strength adhesives. Structuring occurs as a result of the incorporation of block copolymers within the epoxy formulation. These AB-type block copolymers are chosen so that block A has a significantly greater miscibility with the uncured epoxy than does block B. Mixed with the epoxy, these polymers arrange themselves into pseudo-micelles in which the immiscible B block forms a segregated core and the miscible A block forms an expanded corona, as illustrated in Figure 1. Osmotic forces and excluded volume insure an even distribution of these micelles throughout the mixture. As cure proceeds, the molecular weight increase of the epoxy drives the further phase separation of the A block. This separation is templated by the arrangement of micelles, resulting in the formation of three essentially pure phases, situated in discrete nanosized domains. These domains comprise a continuous epoxy network and the sequentially separated domains of the A and B blocks. At a sufficiently high loading of block copolymer, phase A is cocontinuous with the epoxy.

The block copolymer used in the EIC epoxy comprises a backbone of epoxy immiscible poly(dimethyl siloxane) (PDMS) with side chains of epoxy miscible poly(ethylene glycol) (PEG). The structure of this polymer is depicted in Figure 2. This polymer was chosen because PEG is capable of dissolving and transporting ions. (A moderate level of ionic conductivity through the epoxy is required to support electrochemical debonding reactions.) One of the most

interesting discoveries of this work is the profound effect that the addition of salt has on the physical properties, and by inference, on the morphology of the curing system. Without the salt, the phase-separated epoxies are weak, opaque, soap-like materials. With incremental addition of salt, the materials become progressively harder, stronger and more transparent.

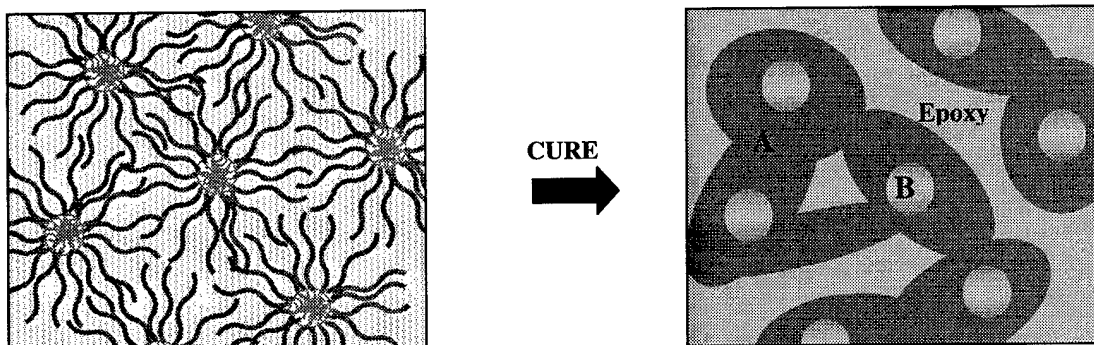


Figure 1: Block copolymer structuring of epoxy resins.

It was originally believed that this effect was caused by the partitioning of ions to the interface between the epoxy and the PEG phase. The salt that produces the best material is ammonium hexafluorophosphate (NH_4PF_6), which to some extent exchanges with the amine curatives to produce ionic charge in the cured epoxy. Segregation of this charge to the interface might be driven by thermodynamically favorable coordination between the charged species and the PEG ether moieties. This coordination could stabilize the interface resulting in decreased domain size, while promoting stress transfer between domains.

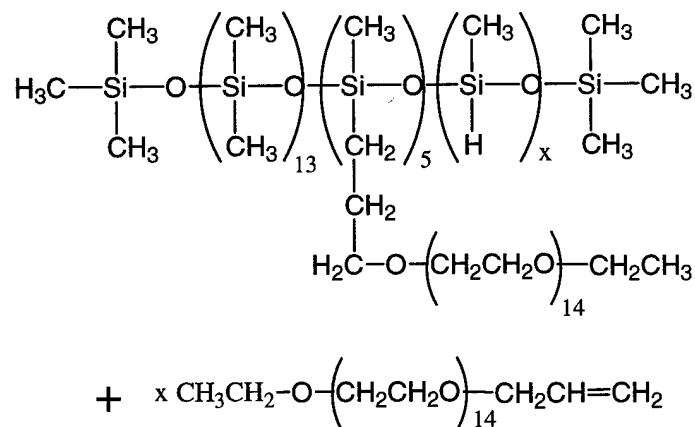


Figure 2: Average molecular structure of PDMS-graft-PEG comb polymer.

More recently, it has been found that it is not the amine moieties of the epoxy network, but rather the unreacted epoxide functionalities that play the dominant role in interfacial stabilization. Unreacted epoxide (oxirane) functionalities are able to coordinate with cations to a greater degree than other ether moieties due to ring constraints and the high dipole moment of the group. In the uncured mixtures, unreacted epoxy groups and PEG molecules can form relatively stable complexes with each other by coordinating with the cations of the salt. However, when the epoxide reacts, it forms a hydroxyl group, which does not show any affinity for cations and is

locally excluded from the vicinity of the cation coordination complexes. Phase separation in these systems is driven not by the increase in molecular weight of the epoxy, but rather by the conversion of epoxy into hydroxyl.

What is interesting about this mechanism is that phase separation is no longer a thermodynamic phenomenon and temperature has much less of an effect on the resulting structure than in the absence of salt. Furthermore, since even the largest molecules present in a partially reacted epoxy still contain a substantial number of epoxide functionalities, premature separation of large species will not occur. Rather, the larger molecules will continuously rearrange themselves to, in effect, bury the offensive hydroxyl moieties, while permitting the unreacted epoxide groups to continue forming complexes with the PEG. Even after gelation, this process continues until stopped by vitrification or exhaustion of reactive functionalities. There may be no actual point at which phase separation occurs in a traditional sense. Instead, the PEG chains may be slowly excluded from the interiors of the developing epoxy network molecules. It is not clear whether the process would lead to a gradient structure or a hard interface. However, there should be a substantial concentration of unreacted epoxy moieties present at this interface, providing interfacial stabilization and stress transfer through cationic coordination complexes.

In studies performed at a number of other laboratories, block copolymers have been used to structure epoxies (4,5,6,7,8) and other thermosetting polymers (9). In the earliest of these studies, an AB block copolymer comprising blocks of PEG and blocks of epoxy immiscible poly(ethylene-*co*-propylene) were used to structure a methylene dianiline (MDA) cured epoxy. Using small angle x-ray scattering and TEM imaging, the researchers found that this system produces a rich assortment of morphologies including lamellar, cocontinuous gyroid, cylinders, spheres and disordered micelles depending on the volume ratio of block copolymer used. However, cocontinuous morphologies were only observed at very high volume fractions of block copolymer (> 60%), a level at which the mechanical properties of the material would be severely compromised. In the EIC epoxy, cocontinuous network formation appears to be the only morphology formed over a wide range of cure temperatures and over a broad formulation window. (In these cases, cocontinuous morphology is inferred from the high strengths of the resulting materials coupled with the moderately high level of ionic conductivity.)

Early on, it was discovered that the EIC epoxies could be adulterated with a number of different organic compounds at a loading of up to 10% by weight, without unduly affecting the thermal or mechanical properties of the resulting cured materials. It is believed that these organic liquids preferentially segregate to the PDMS or PEG domains depending on polarity. These liquids, of course, have no effect on the epoxy (plasticization) when located within these other domains. While segregation of nonpolar species away from the epoxy and into the PDMS is rather straightforward, the controlling factors for partitioning of more polar liquids between the epoxy and PEG phases was less well understood. It is now known that the mechanism that controls phase separation in these salt filled systems also controls the partitioning of polar liquids. Those containing functionalities that can coordinate with cations, such as nitrile or carbonate, will preferentially partition into the PEG phase. Those that do not, such as alcohols, will end up in the epoxy phase. Naturally, each substance will be present to some extent in each of the three domains and will only partition between the three domains following these rules.

Self-healing monomers added to the unreacted mixtures were expected to similarly partition between the three domains. The strategy was to preferentially locate the monomers within a domain that was modified to inhibit polymerization by covalent attachment of inhibitors. These monomers would of course freely diffuse into each of the other domains and, separated from the immobile inhibitors, would be free to undergo polymerization in these other domains. However, large amounts of monomer would only be able to accumulate away from the inhibitor if a void were present. An added advantage of a void produced by mechanical damage would be the large concentration of free radicals that would be present due to the rupture of covalent bonds during void formation. These could be used to initiate polymerization of vinyl or acrylate monomers used as the self-healing agents.

3.0 TECHNICAL RESULTS

3.1 Characterization of EIC Laboratories' Nanostructured Epoxy

The formulation of EIC Laboratories' nanostructured epoxy is provided in Table 1. In addition to the PDMS-g-PEG comb polymer, this formulation features a standard aliphatic amine-curing agent, tetraethylene pentamine (TEPA) which allows rapid cure at low temperatures and a standard epoxy resin, the diglycidyl ether of bisphenol A (DGEBA). These ingredients are relatively inexpensive and allow the resin to be used in the large-scale fabrication of composites using common manufacturing procedures. Also present in this formulation is the electrolyte, ammonium hexafluorophosphate (NH_4PF_6) and a reactive PDMS oligomer. This last component is used to adjust the hydrophilic-lypophilic balance of the mixture. During the course of the present study, it was found that the addition of a small amount of this material was necessary for achieving good and reproducible structuring. It also allowed the mixtures to be degassed without disrupting the structuring emulsions.

Table 1: Formula for aliphatic amine cured nanostructured epoxy.

<u>Ingredient</u>	<u>Description</u>	<u>Amount (by weight)</u>
PDMS- <i>graft</i> -PEG	Structuring Block Comb Polymer	75 parts
Ammonium Hexafluorophosphate	NH_4PF_6 electrolyte	25 parts
Epoxy terminated poly(dimethyl siloxane) (PDMS-epoxy)	Structuring Aid	10 parts
Diglycidyl Ether of Bisphenol A (DGEBA)	epoxy	100 parts
Tetraethylenepentamine (TEPA)	Amine Curative	16 parts

As an initial step in this research, the nanostructured epoxy developed by EIC Laboratories was characterized to determine the morphology of the cured material and verify the cocontinuity of the epoxy and PEG domains. Characterization was performed at MIT under Professor Vander Sande, using TEM and energy dispersive x-ray analysis (EDAX). This latter test was fairly

straightforward and indicated a uniform distribution of elements within the cured material down to the micron scale. Unfortunately, characterization by TEM took substantially longer than was planned due to difficulties in staining the samples and problems with the purity of the structuring block copolymer used in these systems. The preferred method for achieving contrast between the several domains present is to stain the materials with heavy metal atoms using ruthenium tetroxide (RuO_4). This reagent reacts with almost all organic species. However, different materials react at different rates and differential staining can be achieved by limiting the time of sample exposure to RuO_4 vapors. In the present system, the PEG was expected to stain first, followed by the aromatic rings of the epoxy and the PDMS was expected to react at a very slow rate. This proved not to be the case, due to the presence of hydride moieties in the PDMS backbone (see Figure 2). These moieties are present in the starting material for this block copolymer and are used as anchoring sites for the attachment of the pendant PEG chains by a hydrosilation reaction. Depending on the manufacturing parameters, this reaction will occur to varying levels of completion. The PDMS-g-PEG block copolymer used in this study (Dow Corning 193 surfactant), while producing the best cured epoxies in terms of strength, were found to be contaminated with a large portion of residual silane moieties, which react rapidly with the RuO_4 , greatly complicating staining efforts. Further complication is added by the unattached PEG chains, which can partition into the epoxy domains. Better results were obtained using a purer PDMS-graft-PEG comb polymer from Degussa, Goldschmidt 5843. Figure 3 provides a TEM image of the cured epoxy formed using this product.

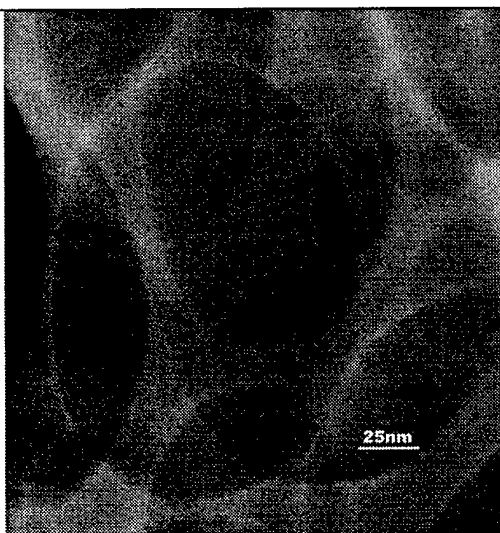


Figure 3: TEM of aliphatic amine cured nanostructured epoxy at a block copolymer volume fraction of ca. 24%.

The large structures seen in this TEM are most likely assignable to a combination of PDMS and PEG domains. There is a high probability that these oblong spheroids are in fact flat disc-like structures. The loading level of block copolymer/salt used in this sample is just below that at which a dramatic increase in conductivity is observed. TEM images of samples made using these higher loadings were too complex to interpret. It does appear that these structures coalesce to form continuous domains. Figure 4 provides a plot of ionic conductivity versus volume fraction of PDMS-graft-PEG. The volume fraction listed also includes the salt and is only an estimate due to difficulties in ascertaining the exact location of the salt in the material. Most certainly, some salt is contained within the epoxy domains. In any case, actual comb polymer

volume fractions are somewhat lower than listed here. What is evident in this plot is a dramatic increase in conductivity at volume fractions between 20 and 30% comb polymer. This appears to be a percolation threshold for the domains seen in Figure 3. Above ca. 35%, increase in conductivity is substantially diminished. This is not what would be expected if a series of morphological transitions were occurring over this range. It is believed that the steep rise in conductivity represents completion of continuity in the PEG domains. This completion occurs at a volume fraction of 37%. Formulations used in the self-healing study were adjusted to this volume fraction so that epoxy content and material strength could be maximized while maintaining free and rapid diffusion of healing agents throughout the material via the PEG network.

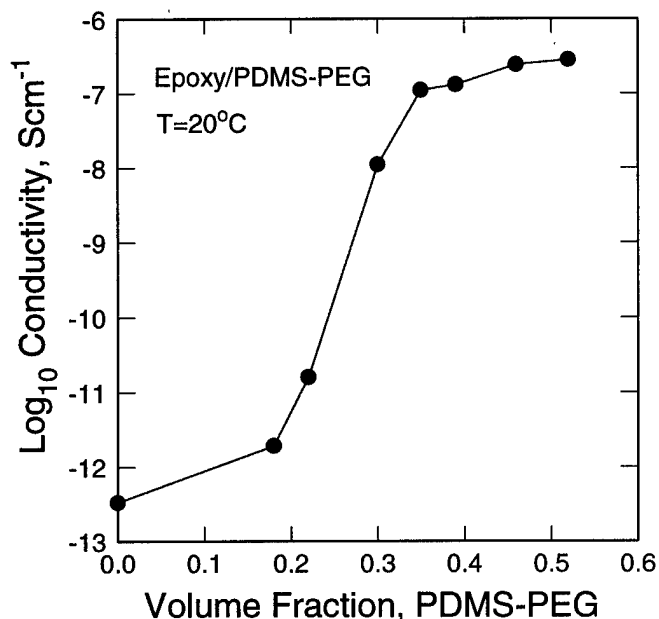


Figure 4: Effect of volume fraction of PDMS-g-PEG/ NH_4PF_6 on ionic conductivity of nanostructured epoxy.

One of the most important accomplishments during this study was the development of a high temperature aromatic amine cured nanostructured epoxy formulation. Not only does this provide the opportunity to fabricate multifunctional composites that can withstand service temperatures in excess of 150°C , it also greatly facilitates the fabrication of these composites by standard manufacturing procedures. These procedures, which include hand lay-up and resin transfer molding were greatly hampered by the short pot-life (rapid room temperature cure) of the aliphatic amine cured system. Development of the aromatic amine cured system consumed a considerable amount of effort and time. The curative of interest, 3,3'-diamino diphenylsulfone, apparently coordinates with salts and hinders phase separation of the PEG and epoxy. MDA, while promoting phase separation, produces a poor structure. Only by combining the two as co-curatives or as 3,3'-DDS with the epoxidized version of MDA (TGMDA) was it possible to achieve the correct structuring. The formulation for this high temperature version is provided in Table 2. A dynamic scanning calorimeter (DSC) trace of a sample of this formulation, which has been cured at 150°C is shown in Figure 5. Evident in the nanostructured material are two glass transitions, one at 170°C for the epoxy network and one at -28°C for the PEG domains. The

temperature scan of an unstructured TGMDA/DDS epoxy sample cured under identical conditions (lower trace) reveals a single T_g at 156°C. The structured material is rigid, mechanically robust, and thermally stable and apparently cures to a greater extent due to the presence of the structuring block copolymer.

Table 2: Formula for aromatic amine cured nanostructured epoxy.

<u>Ingredient</u>	<u>Description</u>	<u>Amount (by weight)</u>
Bis(N,N-diglycidyl methylene dianiline (TGMDA)	epoxy	100 parts
3,3'-Diamino sulfone (DDS)	Aromatic Amine Curative	60 parts
PDMS- <i>graft</i> -PEG	Structuring Block Comb Polymer	97.5 parts
Sodium Hexafluorophosphate	NaPF ₆ (electrolyte)	25 parts
Epoxy terminated poly(dimethyl siloxane) (PDMS-epoxy)	Structuring Aid	32.5 parts

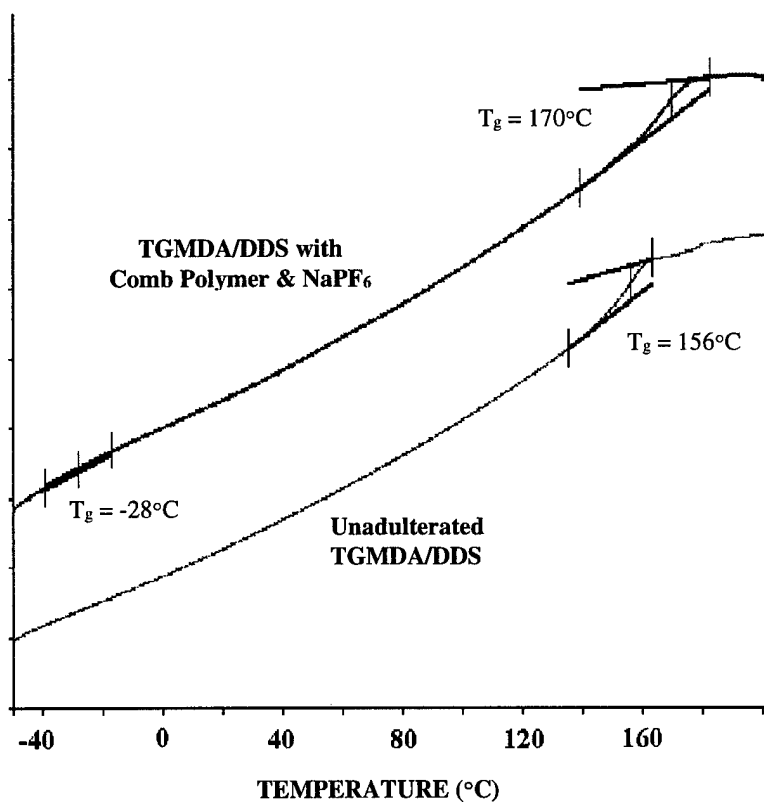


Figure 5: DSC Temperature trace of aromatic amine cured nanostructured epoxy.

3.2 Development of a Self-healing Monomer System

A set of criteria for candidate self-healing agents was developed. This includes 1) monomers must be low vapor pressure mobile liquids at both cure and service temperatures, 2) the monomers must be unreactive toward epoxy, amine and other ingredients used in the nanostructuring formulations, 3) a mechanism of polymerization inhibition must exist capable of functioning at 80°C (with a goal of 150°C), 4) the monomers must preferentially locate within the PEG or PDMS domains and 5) the monomers must have a low toxicity.

Tests were conducted in which monomers were added to curing epoxy mixtures at a loading of 5-10% by weight. Aliphatic amine formulations, which cure at 80°C, were used in these initial studies, to aide in exploring mechanisms for monomer survival. Where needed, an inhibitor comprising dinitrobenzene covalently attached to a large PDMS chain was incorporated into the mixtures. The mixtures were then cured using standard conditions. The cured materials were then subjected to analysis by DSC in order to determine adverse effects of monomer incorporation on T_g . Attempts were also made to look for evidence of reaction between the monomers and the reactive species of the epoxy. Following these tests, samples of successful combinations were pulverized and then Soxhlet extracted using either dichloromethane or hexane. The extracts were analyzed by gas chromatography/mass spectrometry (GC-MS), Fourier Transform Infrared Spectroscopy (FTIR) and RAMAN spectroscopy in order to qualitatively determine monomer survival. Where appropriate, an effort was made to quantify the monomer using the same procedures along with calibrated standards.

A number of monomer systems were analyzed in order to survey the parameters governing incorporation. Monomers comprised acrylates, vinyl esters, vinyl ethers and functionalized PDMS oligomers. Some specific adverse chemical reactions were encountered. Most notable is the Michael addition of amine curative to the acrylates. While this chemical reaction is well known, its occurrence in the nanostructuring epoxy mixtures cannot be predicted a priori. Many reactions, such as thiol/epoxy addition, for instance, do not occur in the presence of these mixtures due to the action of the NH_4PF_6 electrolyte. This salt can inhibit nucleophilic substitutions by protonating nucleophiles. Aliphatic amines generally overwhelm this inhibitory process. However, as the mixtures cure, the residual amines become progressively less reactive. It is possible to get survival of acrylates in partially staged mixtures.

One of the more interesting family of monomers investigated in this study is the vinyl ethers. These monomers are extremely stable toward free radical polymerization. Generally, they will only co-polymerize with acrylates and other electron deficient monomers. During this study, several higher molecular weight vinyl ether monomers were subjected to a temperature of 150°C for several days. No degradation or evidence of polymerization was observed. When these same monomers were exposed to small amounts of ammonium hexafluorophosphate they polymerize rapidly, often with a vigorous exothermic reaction. But, when exposed to a large amount of this electrolyte dissolved in the comb polymer, these monomers revert to their old stable characteristics. It was hoped that advantage could be taken of this property. Monomers, sequestered within the confines of the nanostructured epoxy would be in intimate contact with a large concentration of NH_4PF_6 salt. However, once these monomers diffused to a void, the effective concentration of salt would drop, especially if the monomer were extremely nonpolar.

Table 3 provides a short list of monomers that were qualitatively determined to survive the aliphatic amine cure of the nanostructured epoxies. These monomers also exhibited the least effect on the thermal and mechanical properties of the resulting materials. Generally, these monomers are very nonpolar and it is expected that all were preferentially partitioned into the PDMS phase of the nanostructured epoxies. Surprisingly, even acrylates can survive the cure provided they are sufficiently nonpolar, as is 2-ethylhexyl acrylate.

TABLE 3: Monomers/oligomers that survive incorporation in nanostructured epoxy.

<u>Monomer/Oligomer</u>	<u>Inhibition</u>	<u>Polymerization</u>
<ul style="list-style-type: none"> • 2-ethylhexyl acrylate, • vinyl-2-ethylhexanoate • vinyl stearate 	Must be coupled with dinitrobenzene functionalized PDMS oligomeric inhibitor.	May be cured by free radicals generated by crack formation or by redox catalyst (Ru/thiol).
<ul style="list-style-type: none"> • 4-(vinylloxy)butyl benzoate • 4-(vinylloxymethyl) cyclohexyl methyl benzoate • Bis[4-(vinylloxy)butyl] terephthalate • Bis[4-(vinylloxy)cyclohexyl-methyl] glutarate • Bis[[4-(vinylloxy)methyl] cyclohexyl]methyl] isophthalate • Cyclohexane dimethanol divinyl ether (CDVE) 	Inhibitors are not required. May be stable to fairly high temperatures, if PDMS-DNB inhibitor is used.	May cure by free radicals or, more readily, by electrolyte initiated cationic polymerization.
PDMS oligomers containing thiol, amine, hydride or vinyl functionalities.	No inhibitor required.	Can only be used as A-A + B-B reactants or in Pt catalyzed cures. These cure mechanisms are not viable in presently formulated epoxy.

In terms of having the least effect on the physical properties of the cured epoxy, some of the best monomers were cyclohexane dimethanol divinyl ether (CDVE) and 4-(vinylloxymethyl) cyclohexyl methyl benzoate. As work progressed, interest was focused on multifunctional reactants in order to insure that the healing monomers would yield rigid "patches". Effort was therefore made to quantify the amount of CDVE that survived the epoxy cure. This was done by comparing extractions with known standards using GC analysis. Initial extracts made using dichloromethane proved to be too complex to resolve. Extractions made using hexane were far more specific, allowing accurate determination of CDVE concentrations to be made. Because of the poor solvating abilities of this very low polarity solvent, it is difficult to determine whether the extraction was complete. However, repeated analyses revealed a recovery of 30-70% of the starting CDVE.

The relatively high vapor pressure of the CDVE was problematic. A certain fraction of the monomer was lost due to evaporation during cure and its long-term survival in the cured epoxy could not be guaranteed. Furthermore, although the CDVE appears to preferentially partition into the PDMS phase of the cured material, a significant fraction of this compound is present in the epoxy phase as evidenced by a reduction in T_g relative to the unadulterated material. These problems led to an effort to synthesize in-house larger difunctional vinyl ethers, which retained the low polarity and high affinity for the PDMS domains of the CDVE. The structures of two of these compounds designated self-healing monomers II & III (SHM II & SHM III) are shown in Figure 6 along with the structure of CDVE.

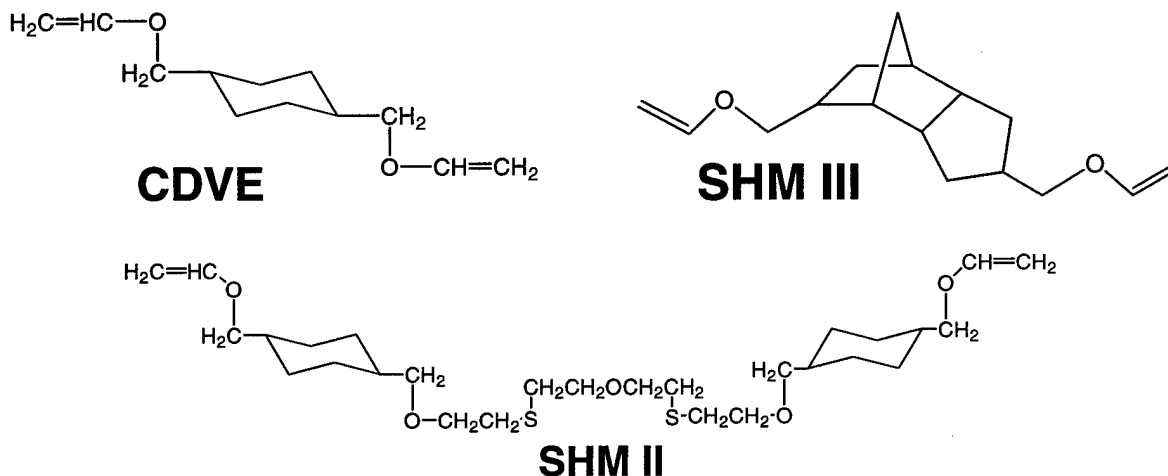


Figure 6: Chemical structures of self-healing monomers used in mechanical studies.

SHM II was relatively easy to synthesize and its structure was verified by GC-MS. The synthesis of SHM III was far less facile. This compound also required vacuum distillation to achieve the purity necessary for this research. However, SHM III proved to be far superior to CDVE and SHM II for the intended purpose because of its low volatility, its existence as a mobile liquid over a broad temperature range, its polymerization into a highly rigid material and its minimal effect on the thermal and mechanical properties of the nanostructuring epoxies in which it was entrained. This latter characteristic is illustrated by the DSC temperature scans shown in Figure 7. Unfortunately, there was insufficient time to generate the quantities of SHM III required for mechanical testing and determination of self-healing functionality in a composite system. For this reason, SHM II was the self-healing monomer solely used in these further studies.

The polymerization mechanism for any of these vinyl ether compounds was tenuous at best. It required the diffusion of the monomer into voids and assumed that under conditions of reduced salt concentration in the voids, spontaneous polymerization of the monomer would occur. This scenario was based on the observation of the behavior of gross amounts of monomer salt and comb polymer and was unsubstantiated for monomer entrained in a cured epoxy. This mechanism could have been verified only by controlled experimentation and the consequent refinements to the formulation that these experiments would have indicated. Since the time required to conduct these experiments was not available, a best guess modified formulation was devised. This comprised SHM II loaded into the nanostructuring aliphatic amine cured epoxy at

a level of 4% by weight. This was accompanied by addition of 4% by weight co-reactant of tetrafunctional thiol. It was known that 1) this reactant can augment the cure of vinyl ethers, 2) this reactant will survive incorporation in the nanostructuring epoxy and cure of that epoxy, and 3) this reactant appears to phase separate into the PEG domains of the epoxy, where it would be for the most part separated from the SHM II monomer until both accumulated in damage induced voids. The self-healing formulations were further augmented by substituting a disulfide-linked epoxy for some of the 5% of the DGEBA used in this formulation. It was believed that these disulfide bonds could insert into any free radical polymerization and in so doing would covalently link the forming self-healing patch with the epoxy network.

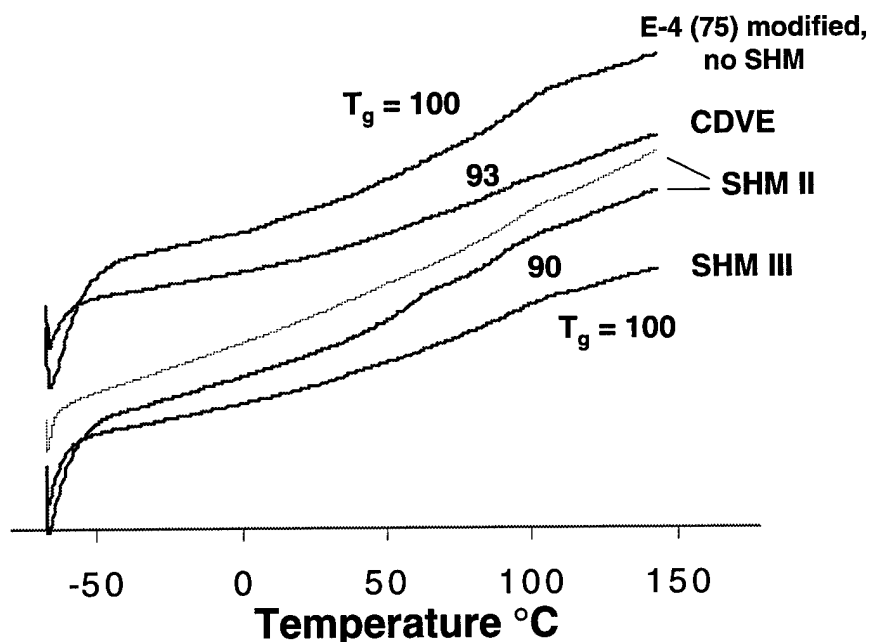


Figure 7: DSC temperature scans comparing the effects of self-healing monomer incorporation on the T_g of nanostructuring epoxies.

3.3 Mechanical Studies and Verification of Self-healing in a Composite

Composites were made using the self-healing system developed above at a number of laboratories including MIT and LMAC using hand lay-up and resin transfer molding fabrication techniques, respectively. In these endeavors, the short pot life of the aliphatic amine cured self-healing mixtures proved to be problematic. Steps such as resin degassing had to be drastically curtailed resulting in poor products. Volumes of mixed resin had to be kept small to prevent runaway exothermic reactions from occurring. Nevertheless, with repeated effort it was possible to generate, using either glass or carbon fibers, a number of composite samples exhibiting the stiffness and mechanical robustness characteristic of epoxy matrix composites.

Verification of self-healing in these specimens was a more difficult challenge. The presence of the second phase provides a resilience to these materials, which prevents mechanical damage from occurring. While the matrix material is macroscopically stiff, it is able to deform at the microscopic level, preventing the usual damage response to impact or overextension

(microcracking). A considerable amount of effort was made to view self-healing in macroscopically fractured samples. These efforts were hampered by the inability of fractured materials to be remated, due to microscopic deformations and the presence of asperities. Because of the low volume of self-healing agent present in any void, no significant space filling capabilities exist in these systems. In some cases, fractured specimens made using self-healing formulations were observed to rebond when held in intimate contact for periods of 8-12 hours. However, the bond strengths were very low, possibly due to poor mating (asperities, etc.). No rebonding was observed in specimens made with unmodified nanostructuring epoxy resin.

Specimens of resin were subjected to repeated cycling in a three-point bend test apparatus at LMAC. This apparatus revealed an interesting increase in stiffness (30+%) that occurs when the samples made using either the self-healing and unmodified nanostructuring epoxy resins are subjected to 30,000 bend cycles at a rate of 10 cycles/second. However, after three days, composites made with unmodified resin revealed a stiffness reduction of 10%, ostensibly caused by accumulated damage. The self-healing specimens, on the other hand, revealed an increase in stiffness of 10% over the same time period. While the cause of the 30% increase in stiffness that occurs after cycling these samples remains unknown, the increase in stiffness of the self-healing mixture relative to unmodified specimens is both real and significant. Whether this can be ascribed to self-healing remains a subject for debate. Other factors besides self-healing could account for the increased stiffness of the self-healing specimens relative to the unmodified specimens. It would have been more convincing if these samples had recovered stiffness after the stiffness had been reduced by mechanical damage.

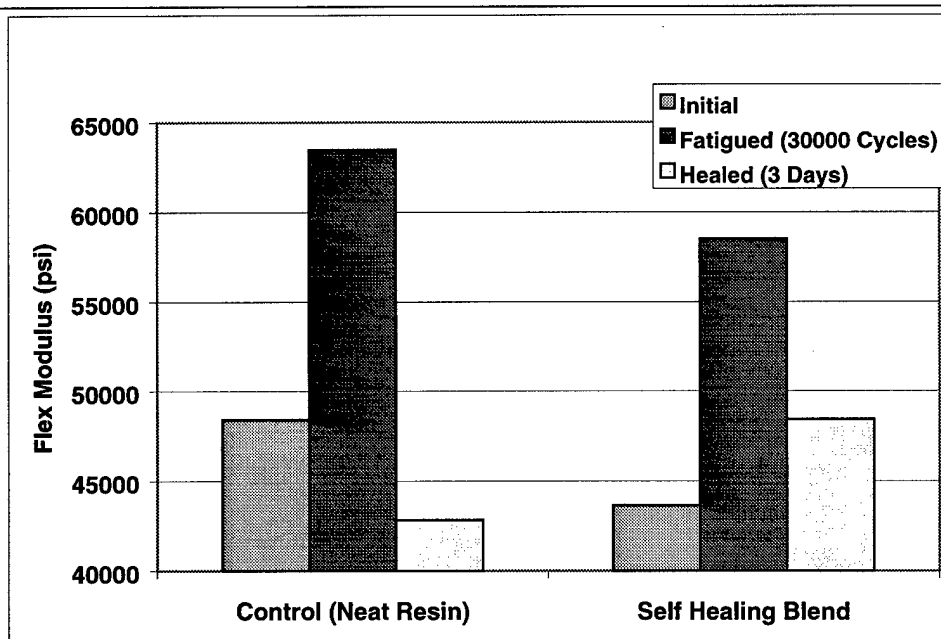


Figure 8: Flexural properties before and after fatigue.

3.4 Further Research

In the time since this research effort was officially terminated, investigation of the electrochemical properties of the nanostructuring epoxies has continued. This was part of the original work proposed for DARPA and has some relevance to this report. Redox reactions can be used to provide sensing functionality to a composite matrix and to some extent during the DARPA funded research effort, the redox properties of intrinsically conducting polymers (ICP) imbedded in the nanostructuring epoxy were investigated. These reactions were rather slow due to the poor ionic conductivity of the resin. It has since been discovered that certain additives, such as 2-cyanoethyl ether (CEE), can be used to augment the conductivity of the PEG phase without affecting the properties of the epoxy. With this increased conductivity, it has been possible to polymerize ICP from monomers entrained within the cured epoxies. Formulations having 4% by weight loading of CEE and 4% loading of ethylene dioxythiophene (EDOT) can be used to bond two pieces of ITO coated glass together. The entrained EDOT can then be electrochemically polymerized onto the interior surface of the glass to yield a film of PEDOT, which can then be switched from dark blue to clear in a matter of seconds.

What is interesting from a self-healing perspective is that this same monomer can be polymerized onto the surface of ITO coated glass that is merely in contact with the surface of the EDOT modified resin and in so doing can be made to adhere to that surface. PEDOT and many other polymers can also be generated at the surfaces of any electrical conductor imbedded in the epoxy. This includes graphite fibers. Thus the opportunity exists to actively polymerize materials at the fiber/resin interface in a composite, so as to heal this interface if damaged or otherwise augment the adhesion between it and the resin. This can be done in a selective manner to tailor the mechanical properties of the composite. It may also be possible to actively control the mechanical response of the composite by selectively switching ICPs at the fiber/resin interface.

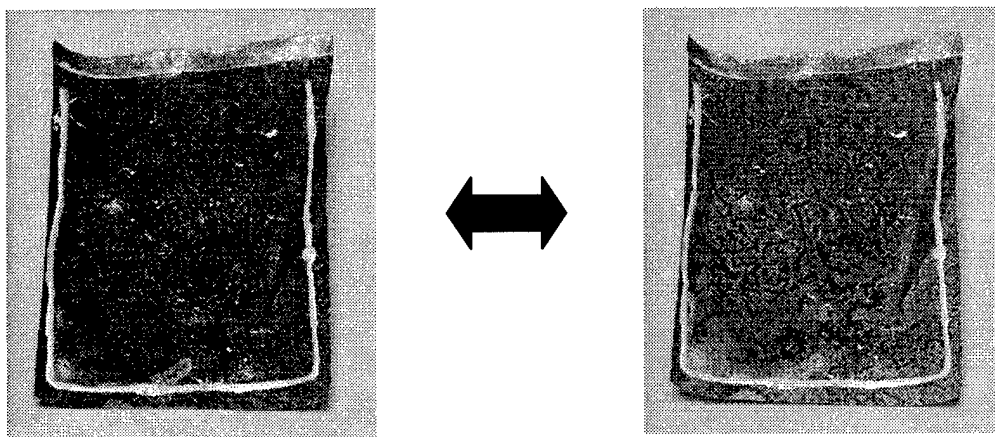


Figure 9: Redox switching of an electrochromic fabric employing the nanostructured epoxy.

The electrolyte properties of the epoxy are illustrated in Figure 9. Here a metallized fabric is coated with a layer of epoxy, followed by a layer of high contrast ICP and a layer of PEDOT. Running a low voltage current between the metallized fabric and the topmost layer of this

material, switches the color of the material between dark blue and red in a matter of seconds. The material is flexible, tough and mechanically and environmentally robust.

4.0 SUMMARY AND CONCLUSIONS

The nanostructured cocontinuous morphology of EIC's epoxy has been confirmed. This structuring has been extended to include resins capable of functioning at temperatures in excess of 150°C. It is possible to incorporate a wide range of monomers within the nanostructured epoxy, cured at a temperature of 80°C. Best results, in terms of survival and minimal impact on the thermal/mechanical properties of the epoxy, are achieved when highly nonpolar monomers are used. It is believed that these monomers are preferentially segregated into the discrete PDMS domains of the nanostructured epoxy. However, these monomers should be free to rapidly permeate throughout the entire material due to an equilibrium partitioning of a small fraction of monomer into the continuous PEG network.

A novel ionically initiated polymerization/inhibition system for vinyl ether monomers has been discovered. This mechanism holds promise for stabilizing monomers constrained within the undamaged epoxy matrix, while allowing rapid polymerization of monomers accumulated in mechanical damage-induced voids. This is especially exciting since these monomers are easily able to withstand extended exposure to 150°C without polymerization or degradation.

This study provided a great deal of promising data supporting the development of self-healing composite systems by the proposed approach. It was, however, severely hampered by time constraints, which demanded an almost instantaneous development of a self-healing system without the necessary supporting research. This time constraint also forced the premature mechanical testing of self-healing formulations before production parameters and characteristics were ascertained by laboratory and before the self-healing mechanism was confirmed. Nevertheless, the results of the study are intriguing. Many discoveries have been made and need to be investigated through careful scientific experimentation to allow this extraordinary technology to be fully exploited.

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