## Identification and Significance of the Problem or Opportunity

This proposal addresses the need for an environmentally acceptable rapidly curing liquid shim for aircraft application by outlining a program to evaluate a rapidly curing epoxy-terminated polysulfide filled with an inorganic compound with mechanical properties similar to crystalline silica. The proposed cure can be controlled by adjusting the ratio of resin to curing agent to range from one minute to the one hour at room temperature based on data available from the manufacture of the epoxidized polysulfide.

The permissible exposure limits for a human carcinogen, during sanding and drilling of the current shim, can be exceeded. In view of this, the proposed material seeks to replace the two part epoxy polysulfide which cures in 8 hours at room temperature and contains particles of crystalline silica to enhance the physical properties and flow characteristics of the sealant. In addition to replacing crystalline silica with a biocompatible filler material, the proposed project seeks an environmentally and occupationally acceptable liquid shim material with the following properties: zero volatile organic compounds (VOCs) and other hazardous compounds; cure time in less than 1 hour; sandable in less than 4 hours; 25 percent flexibility between -65° F and 250° F; and be resistant to standard aircraft fluids.

Epoxidized polysulfides (EPS) are attractive in the proposed application because they possess the following features:

1. very good adhesion to most surfaces; chemical resistance to many dilute acids, alkalis and solvents;
2. mechanical stability and durability;
3. high speed of curing at ambient temperature;
4. lack of sulfur end groups leads to absence of the typical smell of polysulfide polymers;
5. as "polymer hybrids," they combine the properties of polysulfides and conventional epoxy resins as single components;
6. their low viscosities allow excellent low temperature handling;
7. and the elasticity of cured EPS is several times higher than those of amine-cured DGEBA epoxies.

With respect to a filler to replace crystalline silica, we have selected those fillers for epoxy resins that confer the same properties as crystalline silica. Specifically, we have collected the data on the effect of various fillers on hardness, compressive strength, modulus and ultimate deformation of cured epoxy resins and identified those that yield similar results. Accordingly, we will evaluate five such fillers in a rapidly curing EPS system. And we will adjust the flow properties through formulation.

## Phase I Technical Objectives

The primary objective of Phase I is to determine the feasibility using an EPS filled with a replacement for crystalline silica as an environmentally acceptable and rapidly curing

liquid shim for aircraft application. In pursuit of this objective, Phase I will answer the following questions:

(a) What is the optimum EPS for this application?
(b) What is the optimum curing agent to provide an acceptable pot life and curing time at room temperature?
(c) Which extender pigments are most suitable and compatible with the selected EPS and curing agent?
(d) What is the pot life of the optimized formulation?
(e) What is the curing time at room temperature?
(f) What is the flexibility of the cured and filled EPS at -65°F?
(g) What is the hardness?
(h) What are the compressive properties strength of the optimized formulation after curing?
(i) What is the resistance of the final formulation to standard aircraft fluids?
(j) Is the formulation environmentally and occupational acceptable?
(k) What is the estimated cost of the product?

The specific technical objectives of Phase I are to:

1. Evaluate and select EPS.
2. Screen several fillers and extender pigments as replacements for crystalline silica
3. Optimize
4. Perform an environmentally analysis of the optimized formulation
5. Prepare the final report.

## Phase I Work Plan

Phase I Work Plan Outline

1) Scope

This work is a comprehensive attempt to demonstrate the feasibility of using an EPS filled with a replacement for crystalline silica as an environmentally acceptable and rapidly curing liquid shim for aircraft application.

2) Task Outline

The work during Phase I is organized along four main tasks as delineated above in the Technical Objectives. These tasks are: evaluation and selection of EPS; screening of several fillers and extender pigments as replacements for crystalline silica; optimization; environmental analysis; and reporting.

3) Milestone Schedule

The relevant milestones are answers to the questions posed in the Technical Objective section of the proposal. It is not possible to give precise dates at the present time because of the iterative nature of the applied research plan. Table 1, however, is a tentative schedule for reaching significant milestones during Phase I.

Table 1 Milestone Schedule

| Milestone | Months following SOW |
|---|---|
| Selection of optimal EPS for this application | 1 |
| Identification of optimal curing agent to provide an acceptable pot life and curing time at room temperature | 1 |
| Selection of extender pigments that are most suitable and compatible with the selected EPS and curing agent | 2 |
| Identification of the pot life of the optimized formulation | 3 |
| Identification of the curing time at room temperature | 1 |
| Determination of compressive properties | 5 |
| Resistance of the final formulation to standard aircraft fluids | 5 |
| Indication that the formulation is environmentally and occupational acceptable | 5 |
| Best estimate of feasibility of concept | 6 |

4) Deliverables
   a. Kickoff meeting within 30 days of contract start.
   b. Monthly progress reports.
   c. Technical review within 6 months.
   d. Final report with SF 298
   e. Prototypes of liquid and cured shim materials.

TASK 1 EVALUATION OF NEAT EPOXIDIZED POLYSULFIDE

1.1 Selection of Epoxidized Polysulfide

The epoxidized polysulfides, shown in Table 2, and all relevant formulation data will be procured from Akzo Nobel. We plan to seek a collaborative effort with this manufacturer in fulfilling the requirements of the proposed project because of mutual interest and the large market for liquid shim materials.

Table 2 Thioplast Types

| Parameter | EPS 15 | EPS 25 | EPS 70 | EPS 350 |
|---|---|---|---|---|
| Structure | Aliphatic | Aliphatic | Aromatic | Aromatic |
| Branching in mol-% | 2 | 2 | 0 | 0 |
| Viscosity in Pa*s (20°C) | 9-15 | 2-3 | 5-10 | 30-40 |
| Oxygen cont. in wt-% | 1.0-1.5 | 2.1-2.9 | 4.6-5.0 | 4.5-5.5 |

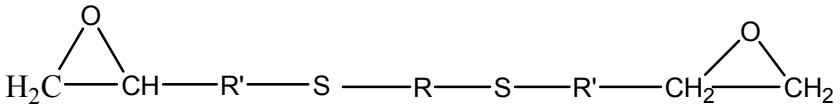
| | | | | |
|---|---|---|---|---|
| Epoxy equivalent in g/equiv | 1100-1500 | 500-600 | 280-350 | 300-370 |
| Density in g/cm$^3$ (20°C) | 1.27 | 1.27 | 1.20 | 1.23 |

EPS-type Thioplast is epoxy-terminated, low viscosity polysulfides. The introduction of epoxy-termination into the polysulfide structure results in formation of a unique polymer which combines the excellent properties of Akzo Nobel polysulfides with desirable features of epoxy-resin systems.

Depending on the field of application Thioplast EPS can either be used alone or in combination with conventional aromatic glycidyl ethers and other epoxies.

Chemistry

In general there are two routes of manufacturing epoxy functionalized polysulfide resins - the reaction of polysulfides with epichlorhydrin or aromatic epoxy resins.
The chemical structure is dominated by the polysulfide backbone – SS-, formal-units and the highly reactive epoxy end groups. Depending on the type of reaction the spacer R' varies.




R= polysulfide structure

$-(CH_2CH_2OCH_2OCH_2CH_2\text{-}SS)_nCH_2CH_2OCH_2OCH_2CH-$

n= 8-20

R' = $CH_2$ or DGEBA/F

Figure 1. Chemical Structure of Epoxidized Polysulfide

1.1 Curing and Evaluation of Epoxidized Polysulfides

Formulation

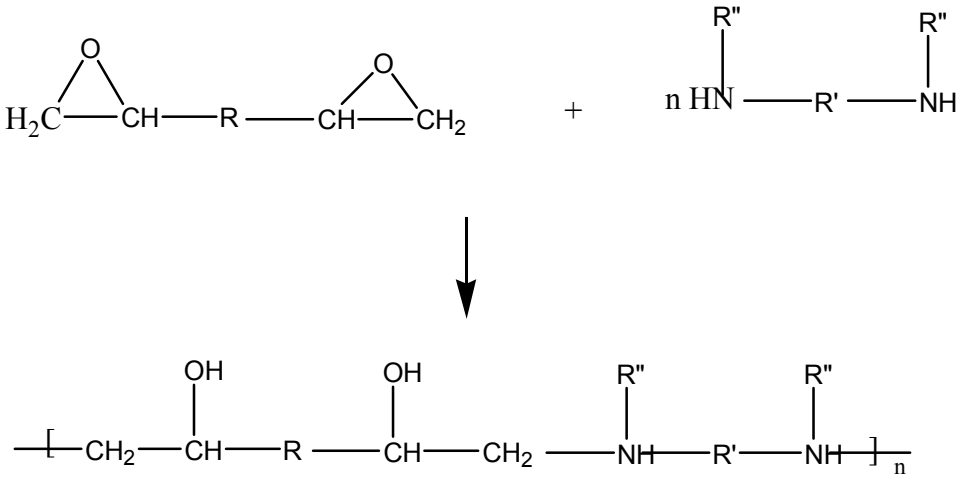
Thioplast EPS–types are commonly formulated as two component systems of which one component contains the Thioplast polymer while the other contains the curing agent. It is our understanding that test formulations for many different applications have been

developed at Thioplast Chemicals and available upon request.

Curing

Thioplast EPS can be cured at ambient temperature down to 0° C. Curing time is dependent on temperature and formulation. The curing agent is in most cases a typical hardener of epoxies as, for example

· aliphatic- amines
· aromatic-amines
· amido-amines
· cycloaliphatic amines
· Mannich bases




R' = aliphatic or cycloaliphatic

Figure 2. Curing reaction of EPS resin with amine curing agent

Since we seek a rapid cure, we will initiate work with DMP-30, 2,4,6-tri (dimethylaminomethyl) phenol, at levels between 1 and 5%. And we fully expect that the desirable cure time will be achieved early in the program.

TASK 2 PRELIMINARY SCREENING OF FILLERS

As replacements for crystalline silica, we will investigate five fillers in comprehensive fashion.

2.1 Aluminum oxide

2.2 Calcium carbonate

2.3 Calcium sulfate

2.4 Lithium aluminum silicate

2.5 Hydrated aluminum silicate

Each candidate will be treated with silane coupling agents with either amino or mercapto functional groups to ensure primary bonding to the polysulfide. Other silane coupling agents will be considered to achieve increased loading of the inorganic fillers. Hence, a discussion of silane coupling agents is warranted.

Silane coupling agents have the ability to form a durable bond between organic and inorganic materials. Encounters between dissimilar materials often involve at least one member that is siliceous or has a surface chemistry with siliceous properties: silicates, aluminates, borates, etc.. This is important because it facilitates the incorporation of other inorganic elements into the shim material. Consider the following:

The general formula for a silane coupling agent typically shows two classes of functionality. $\mathbf{R\text{-}(CH_2)_n - Si - X_3}$

R is of course the organofunctional group, such as the acrylic moiety, and X is a hydrolysable group typically alkoxy, acyloxy, halogen or amine. Following hydrolysis, a reactive silanol group is formed and it can condense with other silanol groups, those on the surface of siliceous fillers, to produce siloxane linkages. Stable condensation products are also formed with other oxides such as those of aluminum, zirconium, tin, and titanium. Less stable bonds are formed with the oxides of boron.

2.6 Nanostuctured Materials

POSS Trisilanol SO1458

Included in this group is polyhedral oligomeric silsesquioxane (POSS) which is a highly soluble and stable trisilanol nanostructured chemical that can also serve as a cure promoter for amine cured epoxy resins. This material is based on POSS nanostructured chemical technology which has two features: (1) the chemical composition is a hybrid, intermediate ($RSiO_{1.5}$) between that of silica ($SiO_2$) and silicones ($R_2SiO$); (2) POSS molecules are physically large ranging from approximately 1-3 nm.

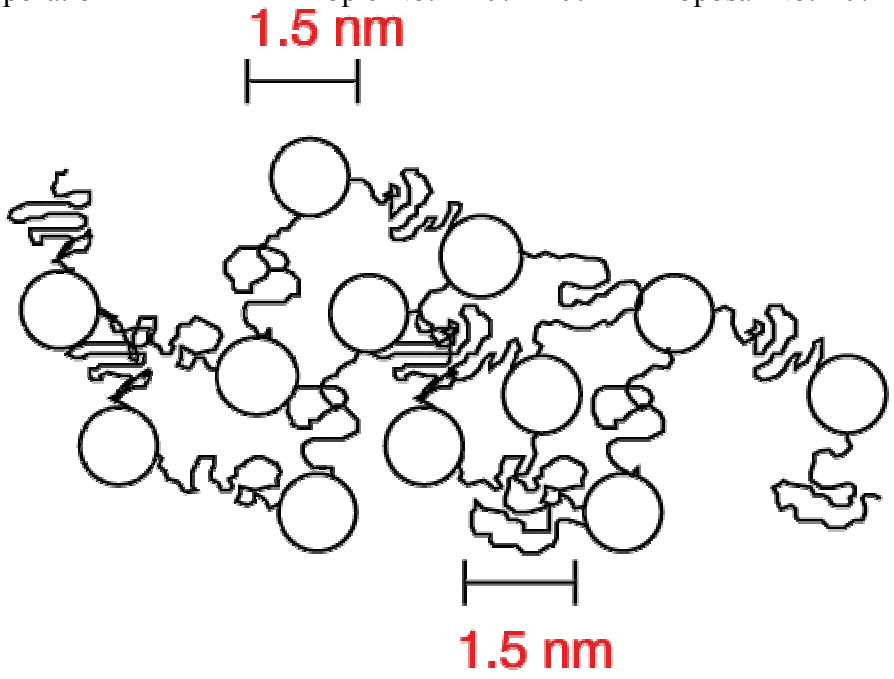



Figure 3. Structural representation of nanostructured POSS material.

The fillers after surface treatment will be mixed with the selected EPS at various levels and (phr) and the uniformly dispersed blend will be mixed with the amine curing agent. In this preliminary screening program, we will identify the optimum filler from the amount of filler needed to yield the same properties as crystalline silica at the lowest level, with minimal effect on cure time and other salient parameters, such as sandability and resistance to standard aircraft fluids.

Data on the effect of filler on compressive properties of a cured epoxy resin is instructive and shown in Table 3. The information was reproduced from one of the best references on epoxy resins (1).

Table 3.Effect of filler on compressive properties of cured epoxy resin (1).

| **Filler, phr** | **Compressive Strength, psi** | **Compressive Modulus, psi x $10^{-6}$** | **Ultimate Deformation, %** |
|---|---|---|---|
| None | 18,500 | 0.500 | 7 |
| Alumina, 300 | 29,700 | 1.000 | 10 |
| Hydrated aluminum silicate, 75 | 20,200 | 0.600 | 10 |
| Calcium carbonate, 175 | 23,900 | 0.900 | 9 |
| Silica, 5µ, 100 | 36,600 | 0.500 | 23 |
| Silica, 30µ, 175 | 29,600 | 0.800 | 11 |

| | | | |
|---|---|---|---|
| Silica, 44μ, 175 | 28,600 | 0.700 | 12 |

Therefore, during this Task, we will prepare cured samples with the selected EPS and the five fillers at 2 different levels. We will send these samples to the Akron Rubber Development Laboratory for the determination of compressive properties according to ASTM D575. Specifically, we will send four specimens of each of 10 samples with a control before proceeding with optimization.

TASK 3. OPTIMIZATION

During this task we will select the optimum filler and use it at varying levels (100, 150 and 200 phr) with the selected EPS and curing agent in three formulations. These will be cured and evaluated as shim materials between composite and aluminum at thicknesses up to 0.1 inch. We will determine the following properties of the filled polysulfide:

3.1 Pot life
3.2 Curing time at room temperature
3.3 Flexibility at -65°F and 250°F
3.4 Hardness
3.5 Compressive Strength, Modulus, and ultimate deformation.

3.1 Pot life

Pot life is defined as the time available for use of the EPS system after the resin and curing agent are mixed. Some systems become progressively more viscous, and for these, in applications requiring low viscosity, pot life generally ends at a viscosity of about 5,000 centipoises at processing temperature. In the proposed application where high viscosities are used, the end of pot life is that point where application is no longer possible.

3.2 Curing time at room temperature

This is the time that system reaches maximum hardness and is sandable.

3.3 Flexibility

The flexibility at -65F will be determined on 0.1 inch thick samples by ARDL.

3.4 Hardness

The hardness of the cured specimen will be determined with the appropriate durometer in our laboratory at room temperature.

The general effect of fillers is to increase the surface hardness of the castings. The effect varies from filler to filler. Alumina, for example, causes a substantial increase in surface hardness.

3.5 Compressive properties

We have elected to send specimens to ARDL for the determination of these on samples before and after immersion in kerosene and hydraulic fluids..

Particulate fillers generally decrease compressive fatigue but increase ultimate compressive modulus and compressive yield strength because of stiffening effect.

TASK 4 ENVIRONMENTAL AND OCCUPATIONAL HAZARD ANALYSIS ON OPTIMIZED FORMULATION

This task entails preparing a material safety data sheet on the liquid shim material. Accordingly, we will prepare material and safety data sheets for the most promising candidates after we have filed patent applications on the proposed technology. Each sheet will contain sections on the following: Material Identity; Proposer's Information; Physical/Chemical Characteristics; Fire and Explosion Hazard Data; Reactivity Data; Health Hazard Data; Precautions for Safe Handling and Use; Control Measures; Label Data; Site Specific/Reporting Information; and Ingredients/Identity Information.

TASK 5 PREPARATION OF FINAL REPORT

At the conclusion of the previous Tasks, we will prepare a final report which will contain discussion of all results with experimental data, conclusions, and technical estimates of feasibility.

## Related Work

There are two reports mentioned in the solicitation that describe manganese curing agents for rapidly curing polysulfides and the application of silicone elastomers. We are confident that an epoxy terminated polysulfide with an amine curing agent will satisfy the requirements and that one of the five fillers will provide the same effect as crystalline silica on the cured EPS.

References

1. Lee, Henry; Neville, Kris; "Fillers for Epoxy Resins,"Handbook of Epoxy Resins, McGraw-Hill, New York, 1982, p.14-20.

## Relationship with Future Research or Research and Development

It is anticipated that rapidly curing EPS materials will be available early during Phase I and that the inorganic fillers selected will show promise as replacements for crystalline silica. Phase II will involve further development, testing of the proposed system to confirm that it meets or exceeds the requirements of aircraft manufacturers. A representative structural component will be identified for actual demonstration in an operational environment. It can be assumed that enough liquid shim material will be available for testing so that it can be placed on the Qualified Products List.

## Commercialization Strategy

The proposer intends to file a patent application because this project is innovative and it attempts to correct a significant problem with liquid shim materials used by the Air Force. The overall market for the resulting technology is a shim material. And manufacture of the proposed material does not present a problem because it involves simple dispersing filler into an epoxidized polysulfide.

We plan to secure a commitment for Phase III that is of the same order of magnitude as the Phase II funding. We expect that this will be adequate to commercialize the proposed coatings after it is placed on the Qualified Products List.

The main driver which supports commercialization is that crystalline silica is a hazardous material. Another significant advantage of the proposed material is rapid curing at room temperature.

A successful demonstration of the feasibility of the concept combined with evaluation in the field by potential users and additional tests by independent laboratories will ensure acceptance by the Air Force. Commercialization of the technology should therefore be successful, if the product is placed on the Qualified Products List.

**Key Personnel**

Dr. Ronald W. Gumbs, a materials scientist with over thirty years of combined academic and industrial experience in the synthesis, characterization and evaluation of polymeric materials, will serve as principal investigator on the project. He was an instructor at the Summer Institute in Polymer Science and Technology at SUNY New Palz, May 21 - June 27, 1979, and has served on the advisory board of the New Jersey Institute of Technology Enterprise Development Center from 1987 to 1997. He is a member of the American Chemical Society Divisions of Polymer Chemistry and Polymeric Materials. He will be assisted by Dr. Chengchang Chen, a polymer chemist.

NAME: **RONALD W. GUMBS**

EDUCATION:
Ph.D. -Chemistry, 1969, SUNY College of Environmental Science and Forestry.
Dissertation on Cationic Polymerization of Nvinylcarbazole
Research Professor: Michael Szwarc
M.S. -Chemistry, 1965, Polytechnic University
Thesis on Cyclopolymerization
Research Professor: Herman F. Mark
B.S. -Chemistry, 1962, Brooklyn College

EXPERIENCE:
RWG Corporation 6/2003 to Present Chief Scientist
Conceived and founded an intellectual property development company with the sole purpose of selling or licensing new technologies.

Gumbs Associates 2/73 to Present President
Developed: dental and medical polymers; heat resistant plastics; coatings and adhesives; encapsulants for silicon solar cells; thin film laminates for solar energy applications; thermoplastic composites for primary structures; and conductive polymers for radar and thermal signature suppression.
Borden Chemical 4/69 to 2/73 Group Leader
Supervised synthesis of wet and dry strength resins for paper; non-aqueous dispersions; conductive polymers; and solventless coatings and inks.
Resin Research Laboratories 6/62 to 9/65 Chemist
Conducted R&D on various polymeric materials and composites.

Publications:

1. R. Gumbs, S. Penczek, J. Jagur-Grodzinski and M. Szwarc, "Simultaneous Cationic Homopolymerizations of Vinylcarbazole and Oxetane", Macromolecules 2, 77-82 (1969)
2. D.F. Paul and R.W. Gumbs, "Solar Energy Collector Coatings from Cyclopolymers of Butadiene and Acrylonitrile", J. Appl. Polymer Science 21, 959 (1976).
3. P. Chandrasekhar, A.M. Masulaitis and R.W. Gumbs, "Novel Synthesis, Spectro-electrochemical, Electrochemical and Chrono-voltabsorptometric Characterization of Poly (Isothianaphthene)", Synth. Met., 36, 303-326 (1990).
4. P. Chandrasekhar and R.W. Gumbs, "Electrosyntheses, Spectroelectrochemical, Electrochemical, and Chronovoltabsorptometric Properties of Family of Poly(Aromatic Amines), Novel Processible Conducting Polymers: I. Poly(Benzidines)", J. Electrochemical Soc., 138, No. 5, 1337-1346 (1991).
5. G.V. Kulkarni, P. Chandrasekhar and R.W. Gumbs, "Electronic Structure of Conducting Polymers," Poster Paper A-5 presented at Gordon Research Conference on Polymers, Wolfeboro, NH, June 24-28, 1991.
6. R.W. Gumbs, "Synthesis of Electrically Conductive Vinyl Copolymers," Synth. Met., 64, No. 1, 27-31 (1994).
7. Y. Wei, J.M. Yeh, D. Jin, X. Jia, J. Wang, G.W. Jang, C. Chen and R.W. Gumbs, Composites of Electronically Conductive Polyaniline with Polyacrylate-Silica Hybrid Sol-Gel Materials, Materials, 7, No. 5, 969 (1995).
8. G.W. Jang, C. Chen, R.W. Gumbs, Y.Wei and J.M. Yeh, Large-Area Electrochromic Coatings. Composites of Polyaniline and Polyacrylate-Silica Hybrid Sol-Gel Materials, J. Electrochem. Soc., 143, No. 8, 2591 (1996).
9. R.W. Gumbs, Polythiophene and Polypyrrole Copolymers, in Handbook of Organic Conductive Molecules and Polymers: Vol. 2, Conductive Polymers: Synthesis and Electrical Properties, edited by H.S. Nalwa, John Wiley & Sons, New York, 1997, pp. 469-504.
10. Ronald W. Gumbs, “Conducting Polymers,” in Encyclopedia of Chemical Processing, edited by Sunggyu Lee, Marcel Dekker, New York, 2006, pp. 526-537.

Patents:

1. M.F. Carty, M.R. Dock, C.P. West, P. Esemplare and R. Gumbs, "Micro-filter for Tobacco Smoke", Fr. Pat. 1,484,033, 9 June, 1967.
2. R. W. Gumbs, "Nonlinear Optical Shield", U.S. Pat. 5,173,811, 22 December 1992.
3. P.E. Esemplare and R.W. Gumbs, "Hot Melt Adhesive Composition that Melts at Relatively Low Temperatures," U.S. Pat. 5,326,413, 5 July 1994.

**Facilities/Equipment**

RWG Corporation has a modern research facility in East Brunswick, NJ with 1,400 square feet of laboratory space and the option to lease more space as the need arises. This facility meets all environmental laws and regulations of federal, New Jersey, and local Governments for the following groupings: airborne emissions, waterborne effluents, external radiation levels, outdoor noise, solid and bulk waste disposal practices, and handling and storage of toxic and hazardous materials. Dr. Ira Whitman of the Whitman Companies serves as an environmental consultant to the proposer.

Specific major pieces of equipment owned by the proposing firm and located in its laboratory in East. Brunswick include:

1. A complete electrochemical research system based on an EG & G Princeton Applied Research (PARC) Model 273 Potentiostat/Galvanostat and Houston Instruments Model 2200GW X-Y recorder.
2. Spectra-Physics Model GCR-11-3 Nd:YAG ns pulsed laser with 2nd, 3rd harmonic generation and pulse compression, associated optics, positioners, two Scientech Model 36-5002 digital power meters, an Antel Optronics Model AR-S1-C custom large-area picosecond photodetector, mounted on a Newport precision optical table. A 2.5 - 7.0 ns, 200 mJ (@ 532 nm) laser pulse repeating at 1 - 15 Hz is available.
3. Instron Model 4201 Universal Testing Machine; a state-of-the-art instrument for measuring mechanical properties of polymeric materials.
4. Perkin-Elmer Model Lambda 3B automated UV-Vis. Spectrophotometer; also used in conjunction with PARC 273 for spectro-electrochemistry.
5. Perkin-Elmer Model 1615 FT-IR.
6. Tektronix oscilloscopes: Model 2210, digital storage, Model DCA 602, pico-second digital storage.
7. Optical train and laser/optic instruments incl. Newport Model C-2001-65ML 65 mW Ar ion laser with acousto-optic (Isomet) modulation, Newport Model M-877 200 ps photodetector, Oriel Model 66165 150 W Xe source, Model 77250 monochromators, associated wavelength controllers, drives, optics, 3-axis positioners. Used for spectroelectrochemical, polymer studies.
8. Denton Vacuum Model 502A high vacuum thermal evaporation system (for thin film semiconductor, metal and other depositions.
9. Resistivity/conductivity and electrical test instrumentation: Signatone Model S301-4 4-point resistivity probe interfaced to Keithley Model 617 electrometer, Keithley Model 220 current source; Keithley Model 197A digital multimeter.

10. Integrated Technologies, Inc. Model P6204 Spin Coater.
11. Power supplies for Electropolymerization: Micronta Dual Tracking and Vector-Viz WP-773A, associated bulk (1 L) synthesis cells.
12. Precision Instruments vacuum pumps and high-vacuum line system.
13. Ovens/Furnaces: Labline IV and Thermolyne F21100 tube furnace (to 1200$^{o}$C).
14. Large capacity LabLine Imperial controlled-temperature system.
15. Ultraviolet light sources for polymerization initiation, related functions.
16. U.S. Stoneware Ball and Jar Mill, Model No. 753 RM/V.
17. Brookfield Viscometer
18. Dymax Model 1200 Focused Beam UV-curing system.

**Subcontractors/Consultants**

No formal subcontracting or consulting is planned during Phase I

**Prior, Current, or Pending Support of Similar Proposals or Awards**

No prior, current, or pending support for proposed work.