REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
November 17, 2000,

3. REPORT TYPE AND DATES COVERED
Draft Final Report

4. TITLE AND SUBTITLE
Non-Autoclave Materials for Large Composite Structures

5. FUNDING NUMBERS

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8. PERFORMING ORGANIZATION REPORT NUMBER
SRL-F-8-2000

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFRL/MLBC
Bldg. 654 Rm 136
2941 P Street
WPAFB OH 45433

10. SPONSORING/MONITORING REPORT NUMBERS

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Report developed under SBIR contract for topic BMDO 00-013. Launch vehicles for the Space Based Infrared System will include Titan Launch vehicles and the Air Force Space Operations Vehicle (SOV). Composite structures on the SOV (the military version of NASA's Reusable Launch Vehicle (RLV) will be too large to cure inside existing autoclaves. Electron Beam processing is one of the most promising approaches for out-of-autoclave composite curing and bonding. Recent technology demonstration programs have shown potential cost savings and the ability to make large parts using EB curing at low temperature. However, additional development of EB-cured materials is required to meet RLV and SOV mechanical and thermal design specifications. Science Research Laboratory and the University of Dayton Research Institute have formulated new EB-cured resins and composites and tested these materials at ambient temperature and in liquid nitrogen. The results show that the electron beam cured materials developed and the electron beam curing process are promising for space structures and for cryogenic applications. Directions for future improvements in thermal and mechanical properties of the resins and the composites are discussed. Additional mechanical testing is required to establish a complete set of mechanical properties in liquid nitrogen and in liquid hydrogen. The ultimate goal is to meet or exceed the properties of Cytec Fiberite 977-2, the baseline used by Lockheed Martin in the NASA X-33 Half–Scale Reusable Launch Vehicle program.

14. SUBJECT TERMS
SBIR Report

15. NMBER OFPAGE
26

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT

18. SECURITY CLASSIFICATION OF THIS PAGE

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

DTIC QUALITY INSPECTED 4

20001211 004

TABLE OF CONTENTS

1. RESULTS OF THE PHASE I PROJECT

The results of the Phase I project are given in bullet format in the next section. This section contains background information, followed by experimental results, conclusions and estimates of technical feasibility. Future research directions are then discussed.

2. EXECUTIVE SUMMARY

- **Electron–Beam (EB) Curing of Large Composite Structures**
  —Out-of-Autoclave
  —Low temperature curing resulting in T_g's higher than the cure temperature
  —Beam energy of 5 MeV penetrates 1 cm carbon
- **EB–Cured Resins and Composites Require Testing at Ambient Temperature (RT) and at Cryogenic Temperature for Space Operations Vehicle Applications**

—EB–cured resins and composites tested for the first time in LN_2

—Resin development required based upon results of cryogenic testing

- **Goals**

  —Evaluate EB–cured composites at ambient and cryogenic temperature

  —Improve EB–curable resins for large composite structure fabrication

  —Fabricate composites and show improvement at low temperature

- **Approach**

  —Highly stiff EB–curable LC resins with low CTE values

  —Second phase toughened resin systems

  —Addition of inorganic nanoparticles with low CTEs

  —First time testing both at ambient temperature (RT) and in LN_2

- **EB–cured composites show promising properties over a range of temperatures**

  —Acrylated epoxy, dual–curing composites prepared by VARTM show interlaminar shear strength(ILSS) up to 8.8 ksi at RT and maintain ILSS in LN_2 - second phase toughened

  —Newly formulated cationic epoxies maintain ILSS of 7.0 ksi in LN_2 compared with 6.9 ksi at RT with primary phase toughener at 70 wt%

  —Free radical model formulation with 25-50% primary phase toughener shows an increase in ILSS of 30 to 35 % in LN_2 compared to RT testing

- **Nanoparticle reinforcement of resin results in 50 to 65 % increase in stiffness at 5 to 10 % loading**

  —Treated clay combined with reactive coupling agent used

  —Low CTE does not change over entire temperature range of interest

- **First EB–cured unidirectional composite prepared with liquid crystal resin in the nematic phase**

  —Composite shows low ILSS, but retains stiffness after 5 cycles between RT and -196°C

  —Improved stiffness likely by applying shear before cure, cure in a magnetic field or modification of chemical backbone of LC resin

- **Future Plans**

  —EB–curable resin development and composite fabrication

  - Extend use of tougheners in free radical and cationic resins, newer materials and higher weight %

- Use nanoparticle stiffeners in composites
- Prepare epoxy acrylate and liquid crystal unidirectional prepregs and fabricate unidirectional composites
- Reformulate dual–curing (thermal/EB) resin into EB–curable resin
  —Resin and Composite testing at RT and in LN_2
- Resin mechanical testing - tensile, modulus and strain to failure, compact tension
- Composite mechanical testing - coordinate with AFRL and PRDA contractors
  — 0°, ±45°, 90° tension, Double Cantilever Beam, End Notch Flexure, microcrack density/first ply failure in [0/90/0]
  —thermal and mechanical testing of quasi-isotropic laminates in LH_2 and compare with PRDA testing by Boeing

3. BACKGROUND

The National Missile Defense System (NMD) and the Theater Missile Defense (TMD) Systems will require the development of high capacity reusable launch vehicles to deploy this system cost effectively. A critical requirement for such launch vehicles is the development of lightweight cryogenic tanks, which can be constructed at low cost. Such lightweight tanks can be constructed from carbon composites cured by electron beams, which offer out–of–autoclave curing and a decrease in their cost.

The NMD and TMD systems as currently envisioned consist of the ground-based interceptor missile systems and the Space and Missile Tracking System (SMTS), also known as Brilliant Eyes. The system will consist of a constellation of small, low-cost, lightweight, low-altitude satellites. A key role of Brilliant Eyes is to support Theater Missile Defense by providing the capability for world-wide tracking of ballistic missiles in flight from launch to re-entry. Brilliant Eyes will provide precise and timely launch point estimates to enable prompt counterstrikes against missile launchers. It will cue ground-based radar to acquire incoming missiles or warheads. Brilliant Eyes will then assess the status of these targets. During peacetime, Brilliant Eyes monitors ballistic missile tests worldwide by collecting threat development, deployment, signature and trajectory data. This allows defenses to maintain and optimize their effectiveness as new threats appear.

SMTS is the low earth orbit component of the Space Based Infrared System (SBIRS) architecture. Its unique capability to track missiles throughout their trajectory - not just during the "hot" boost phase - allows the system to effectively cue missile defense systems with accurate targeting data. It is particularly useful to National Missile Defense and against the longest-range theater missile threats. SMTS also has the potential to address other SBIRS requirements, such as Technical Intelligence and Battlespace Characterization. A SMTS constellation optimized for national missile defense would consist of 21 satellites in three orbit planes. One optimized for all four SBIRS missions would contain at least 28 satellites in four orbit planes.

The baseline SBIRS architecture includes satellites in Geosynchronous Earth Orbit (GEO), Low Earth Orbit (LEO), and sensors hosted on satellites in Highly Elliptical Orbit (HEO). These satellite systems are to complement, and eventually replace, the Defense Support Program (DSP) system that has been the corner stone of US reconnaissance since the early 1970's. Historically, DSP satellites have been launched atop the Titan III & IV family of launch vehicles; one was launched aboard the Space Shuttle. Currently, DSP satellites are launched into geosynchronous orbit using a Titan IVB launch vehicle with an Inertial Upper Stage. DSP-16 launched aboard NASA's Space Shuttle mission STS-44 (Nov. 24, 1991). The satellite remains dually compatible with both the shuttle and Titan IV launch systems. After release from either the Titan or Shuttle, the satellite is boosted into an intermediate transfer orbit using an Inertial Upper Stage commonly referred to as an IUS. Launch vehicles for the SBIRS will include Titan vehicles and the Air Force Space Operations Vehicle (SOV). The SOV is the military version of the NASA Reusable Launch Vehicle (RLV). The SOV will be designed to fly four times as many missions as the RLV. Both the RLV and SOV fleets will have large LH_2 composite cryogenic fuel tanks, but the cryogenic tanks on the SOV will experience higher service temperatures and g forces than those on the RLV. A primary mission of the SOV will be to support and maintain the SBIRS system. The relationship between the SOV and the SBIRS as envisioned in the US Space Command Long Range Plan is shown in Figure 1.

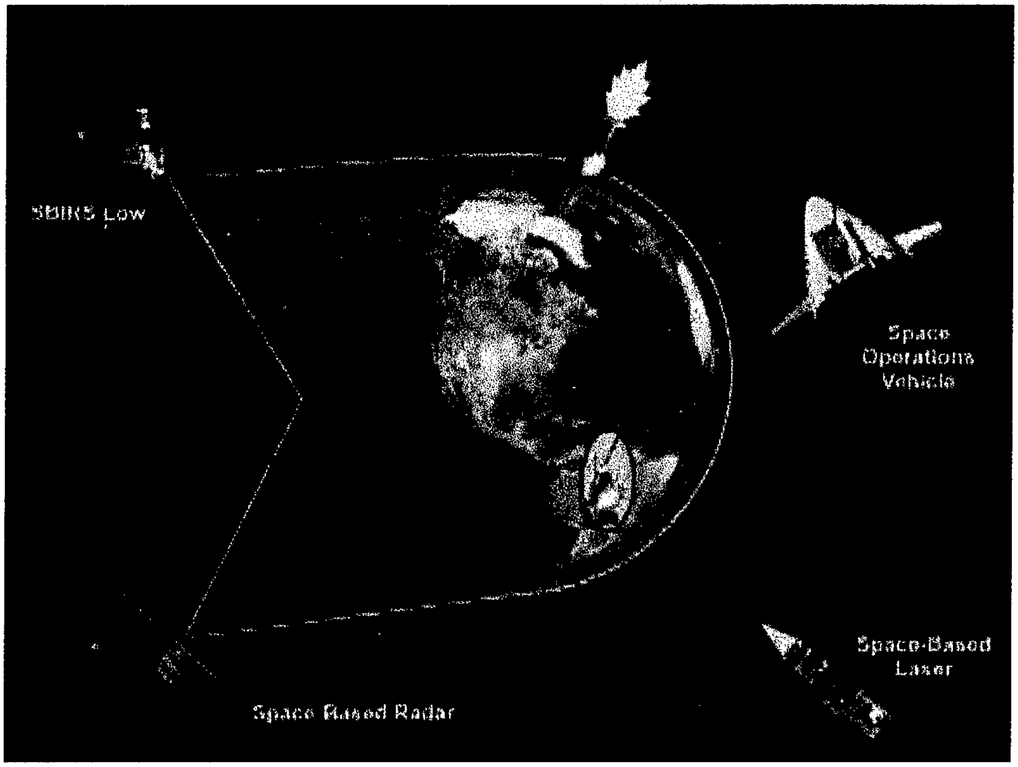


Figure 1. Key Tasks for Missile Defense (From Global Engagement, United States Space Command, Long Range Plan, Revised April 1999)

Over the next decade, NASA and the Air Force plan to build reusable launch vehicles for civilian and military missions. These vehicles will incorporate large composite structures that are too large for existing autoclaves and need to meet very stringent mechanical and thermal requirements. The out-of-autoclave materials and processes described in this report, when fully developed, have the potential to significantly reduce the cost of fabricating these structures while still meeting the operational requirements.

The two leading out-of-autoclave approaches are low-temperature thermal cure systems and–beam–curable systems. Electron–beam processing is well suited for curing of large cryogenic tanks. EB-curable towpreg and prepreg materials have long shelf lives and cure only when radiation is applied. Long heat-up and cool-down steps for composite curing, as well as thermal mismatch issues, are avoided by using the highly energetic electrons at ambient temperature. Glass transition temperatures significantly higher than the cure temperature are observed. Although EB–curing has considerable promise for this application, EB-curable materials do not yet have the necessary properties to fabricate the RLV and certainly not the SOV cryogenic tanks. This is true both for the resins needed in the composites and the adhesives. The properties of Cytec Fiberite 977-2 thermally cured resin and composite is compared with the properties of electron–beam–cured resins and composites in Table 1. The 977-2 toughened system was selected by Lockheed Martin as the baseline material for the X-33 RLV program. It is recommended by the manufacturer for cryogenic applications and is more highly toughened than 977-3. In this Phase I project, recently formulated composite resins have been used to fabricate woven and unidirectional composites. The electron–beam–cured resins and composites have been tested at ambient temperature and in liquid nitrogen for the first time.

Table 1. A comparison of properties of the 977-2 specified for the X-33 cryotanks with the properties of EB–resins and composites available at the start of Phase I.

Resin Property	**Cytec Fiberite 977-2**	**SRL Dual–Cured Epoxy Acrylate**	**Applied Poleramic Cat B EB–Cured Cationic Epoxy**
T_g (°C, DMA)	212	134-190	180
Service Temperature(°F)	260 dry 220 wet	Not established	Not Established
Cure Temperature (°C)	177	EB at ambient	EB at ambient
Tensile Strength, ksi	11.8	8	9.7
Tensile Modulus, msi	0.51	0.5	0.57
Flexural Strength, ksi	28.6	18	12.5
Flexural Modulus, msi	0.5	0.53	Not reported
K_{1C}, ksi $\cdot$in$^{1/2}$	1.22	Not reported	0.4
G_{1C}, in-lb/in^2	2.7	1.9	Not reported
Composite Property	**IM Unitape**	**Woven AS4 5HS G'**	**Woven AS4 5HS**
Tensile Strength, ksi	390	99	100
Tensile Modulus, msi	24	10	Not reported
Flexural Strength, ksi	Not reported	100	125
Flexural Modulus, msi	Not reported	8	Not reported
Compressive Strength, ksi	230	71	Not reported
Compressive Modulus, msi	22	9	Not reported
G_{1C}, in-lb/in^2	2.7^b	1.9	Not reported
Short Beam Shear, ksi	Not reported[1]	8	8

[1] The tensile shear strength of 977-3 is 16ksi[1].

4. EXPERIMENTAL RESULTS

The objectives of this SBIR program were to (1) select promising electron–beam–curable composite resin formulations for cryogenic applications and prepare composite panels from them; (2) perform mechanical testing on the cured resins and composites at ambient temperature and in liquid nitrogen; (3) select the most promising materials for reformulation, additional cryogenic testing and scale-up in Phase II. The materials selected for Phase I were based upon three concepts: (1) model highly stiff resins with coefficient of thermal expansion approaching to those of the fibers; (2) second phase toughened resin systems with one phase capable of expansion and contraction at reduced temperatures; and (3) utilizing nanoparticle fillers with coefficients of thermal expansion (CTEs) closer to that of the fibers over the entire temperature range of interest. All the objectives of the Phase I program were met. The most promising approaches include composite resin formulation utilizing both primary and secondary phase toughening together to optimize both low and high temperature properties and the use of fillers with CTEs that do not change over the entire temperature range.

4.1 Coefficients of Thermal Expansion

The coefficients of thermal expansion (CTEs) of carbon fibers are considerably different than those of organic composite resins. This property of the materials is one major problem for applications where thermal cycling over a wide range of temperatures is required. Temperature ranges from the boiling temperature of liquid hydrogen (20°K, –423°F) to at least 250°F for NASA's RLV and 350°F for the Air Force SOV. Differences in the CTE between the carbon fibers and the resins over these temperature excursions cause microcracking to occur. Microcracking causes deterioration of mechanical properties and leaking of the contents of a cryotank prepared from the material. For this reason, the CTEs of fibers, conventional polymers and EB–cured resins were measured. The results are shown in Table 2.

The CTEs of anisotropic materials such as fibers differ in the axial and transverse direction. In the axial direction, the values are near zero, but slightly negative. In the transverse direction, the values are near 10, compared to about 50 to 80 for conventional composite resins. The anisotropic liquid crystal (LC) resin exhibits a CTE in the parallel direction that is closer to that of the fibers than any other resin tested, but is rather large in the direction perpendicular to the orientation of the LC. The LC tested has a methyl substituent on the aromatic rings in the backbone, contributing to the CTE in the perpendicular direction. The methyl group lowers the transition temperature from crystalline to nematic and so offers a resin processing advantage.

Table 2. Linear Coefficients of Thermal Expansion of Fibers and Resins.

Material	Coefficient of thermal expansion (ppm/°C)
Carbon fiber low modulus	–0.7 (axial direction), 10 (transverse direction)
Carbon fiber high modulus	–0.5 (axial direction), 7 (transverse direction)
S-glass	1.6 (glass bars)
Polymethyl methacrylate	70 (0 to 50°C)
Polyimide	60 to 80
Epoxy Resin	54 (at 25°C)
PTFE	99 (25 to 300°C)
SRL Electron–Beam–Cured Resins (No Postcure)	
UDRI LC (RM257 with the C3 spacer replaced by C6	–17 to +8 (25 to 40°C, parallel to thermal alignment) 180 (perpendicular to alignment)[2]
SRL 104 epoxy acrylate	43 (–140 to 30°C), 172 (>68°C)
SRL 582 urethane acrylate	70 (–140 to –60°C), 206 (–39 to 120°C)
SRL 1-104/1-582	55 (–140 to –30°C), 172 (9 to120°C)
SRL 90047	43 (–140 to 30°C), 97 (60 to 120°C)
SRL 3-90047/1-582	50 (–140 to 0°C), 122 (40 to 120°C)
SRL 1-90047/1-582	57 (–140 to –30°C), 157(30 to 120°C)
SRL 299/BMI	98 (–105 to 55°C)
SRL VCCM-4	48 (–140 to 40°C) dual curing second phase toughened epoxy acrylate 185 (80 to 120°C) from the University of Delaware
SRL KB-2	88 (–105 to 55°C) second phase cationic epoxy with 15% toughener from Applied Poleramic
SRL KB-3	108(–105 to 55°C) second phase cationic epoxy with 30% toughener from Applied Poleramic
SRL KB-4	60(–140 to 20°C) primary phase toughened cationic epoxy containing 70% rubber from Applied Poleramic 223 (70 to 120°C)

The CTEs of the electron–beam–cured resins were measured using thermomechanical analysis over the temperature range from –140°C to +120°C. Many of the resins exhibit CTEs near that of thermally cured epoxy resin, followed by larger CTEs in the 100 to 200 range above a thermal transition that occurs during the thermal scan. These transitons are most likely due to T_g's of components of the resin formulations, probably the toughening compound. Finding a toughener with a low CTE is an important step toward minimizing the thermal expansion of the resin. Thermoplastic tougheners, for example, have higher T_g's and so are potential tougheners with lower CTEs in the temperature range of interest.

4.2 Polymers With Low T_g's

Another serious problem with use of composites at cryogenic temperatures is that all organic polymers and also the inorganic silicon and phosphorous polymers are brittle at cryogenic temperatures corresponding to the boiling point of liquid nitrogen (–196°C) or below. A survey of the glass transition temperatures of polymers is summarized in Table 3. The materials shown were selected from the Polymer Handbook [3] and include examples from all classes of polymers with Tg's below –70°C. This information was utilized in the formulation of the resins that were used in this program. While still not low enough to be rubbery at cryogenic temperatures, tougheners with low T_g's will reduce brittleness when cold. There are several types of tougheners that can be used individually or in combinations, with tougheners from another class. Secondary phase tougheners are not soluble in the untoughened resin and exhibit phase separation that can be detected by X-ray techniques. Primary phase tougheners are soluble in the resin and do not show phase separation. Both the primary and secondary phase tougheners can be rubbery tougheners or thermoplastic tougheners. Just one toughener has been used in Phase I, but mixtures will be used in future studies. The mixtures can include both reactive and unreactive tougheners in the resin formulation, with or without functional groups such as acrylates or epoxies.

Table 3. A List of Polymers with Low T_g's that are Potential Rubbery Phase Materials for Cryogenic Composites.

Polymer	**Thermal transition temperature, °K (°C)**
Poly(butadiene), cis	164 to 171 (–109 to –102)
Poly(ethylene)	148 (–125) small change in heat capacity, the lowest of four transitions, the others at –80°C, –20° and 60°C
Poly(methylene)	155 (–118)
Poly(3-methoxypropyl acrylate)	198 (–75) methyl ether substituent group
Poly(4-thiahexyl acrylate)	197(–76) contains sulfur
Poly(N-dodecylacrylamide)	198(–75) amorphous sample
Poly(N-octadecylacrylamide)	162(–111) side chain with 18 carbon atoms
Poly(decyl methacrylate)	203(–70) side chain with 10 carbon atoms
Poly(octadecyl methacrylate)	173(–100) side chain with 18 carbon atoms
Poly[oxyhexyl(oxymethyl)ethylene	190(–83) polyether side chain
Poly(oxytetramethylene)	189(–84) polyether with MWs of 1000 and 2000 used in polyurethanes with low T_g's
Poly(hexyloxyethylene)	199(–74) hexyl side chain
Poly(oxytetramethyleneoxyadipoyl)	155, 194 to 206(–118, –79 to –67) polyester with MWs of 1000 and 2000 used in polyurethanes with low T_g's
Poly(oxytetramethyleneoxycarbonylimino–1,4–cyclohexylenemethylene–1,4–cyclohexyleneiminocarbonyl	198(–75) an aliphatic polyurethane, the polyurethane used in UV 582, described later in this report
Poly(dimethylsiloxane)	146(–127) one of a series of inorganic backbone polymers that may have compatibility problems with composite resins
Poly(diethoxyphosphazene)	189(–84) one of a series of inorganic backbone polymers that may have compatibility problems with composite resins

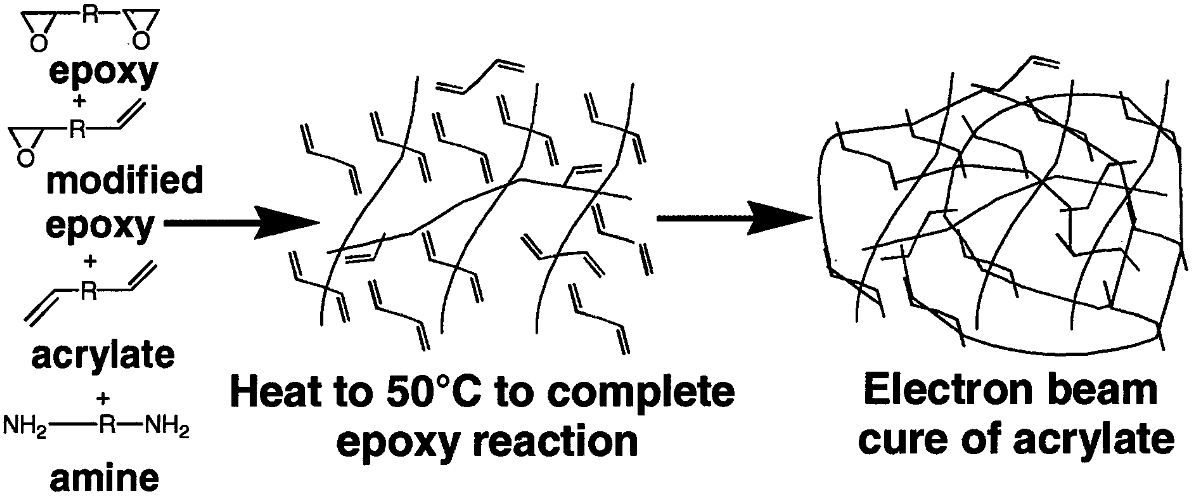


Figure 2. Epoxy acrylate resins are formulated for dual cure. The epoxy reacts with the diamine at 50 to 80 °C. Electron–beam–curing of the acrylates by a free radical mechanism takes place after the thermal step. A small number of double bonds remain unreacted.

4.3 Resin Formulations

4.3.1 Dual-Curing Resins

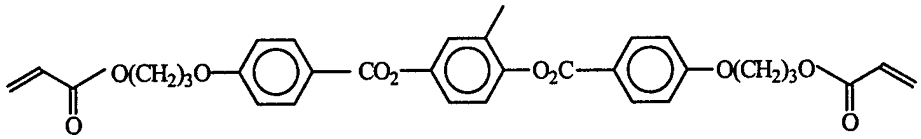
The dual–curing epoxy acrylates have several advantages, including low moisture absorption compared with epoxies alone. They exhibit reduced shrinkage compared with conventional acrylates due to the reduced number of double bonds compared to the total weight of the resin. These radiation curing free radical resins are not inhibited by the presence of other chemical compounds, unlike the cationic curing resins that are inhibited by nucleophiles [4]. The epoxy acrylates are compatible with commercially available fiber finishes, many of which contain nucleophiles such as amines. The epoxy acrylates can be cured in the presence of thermally cured commercial resins and adhesives. The epoxy acrylates are compatible with a wide variety of tougheners for composite resins, including those containing nitrogen such as the workhorse carboxy terminated butadiene acrylonitriles. The dual–curing resins are useful in applications where out–of–mold electron–beam–curing is used because mold material costs are reduced. For applications where external molds are not used, such as filament winding or fiber placement, the epoxy acrylate can be reformulated for electron–beam–curing alone. The properties of these resins and woven S-2 glass composites were measured previously and are summarized in Table 4[5]. The epoxy acrylate exhibits a Tg of 130°C as formulated and T_g's up to 190 °C have been observed when a partially methacrylated trifunctional epoxy is used in the formulation. The dual–curing epoxy acrylates retain 90% of their properties after aging at 50°C and 85% relative humidity until equilibrium moisture uptake is reached.

Table 4. The properties of dual–curing composites exceeded those of vinyl esters when prepared with woven S-2 glass treated with Fiberite 933 sizing. The urethane acrylate and the epoxy acrylate resins were untoughened.

	Vinyl Ester (Baseline)		Urethane Acrylate (EB Cure)		Epoxy Acrylate (EB Cure)	
Property	**Strength (ksi)**	**Modulus (msi)**	**Strength (ksi)**	**Modulus (msi)**	**Strength (ksi)**	**Modulus (msi)**
Tensile ASTM D3039	82.2 ± 4.1	3.13 ± 0.13	81.8 ± 2.5	3.96 ± 0.15	81.4 ± 2.9	3.83 ± 0.06
Compression ASTMD3410-87 Procedure B: IITRI	41.8 ± 2.6	3.94 ± 0.24	66.1 ± 2.6	4.13 ± 0.07	54.0 ± 2.5	4.3 ± 0.14
Shear – Iosipescu	12.2 ± 0.25	0.88 ± 0.37	14.5 ± 0.83	1.05 ± 0.11	14.7± 0.80	1.07± 0.19
Short Beam Shear ASTM D2344-84	4.67± 0.11	---	7.30 ± 0.29	---	6.89 ± 0.66	---
Flexural – ASTM D790-86	55.7 ± 3.1	---	93.1 ± 6.8	---	71.0 ± 3.9	---

4.3.2 Liquid Crystal Resins

A liquid crystal resin was selected as a model system for highly stiff resins. The CTEs of a chemically similar resin are shown in Table 1 in the parallel and perpendicular direction to the alignment of the resin in a magnetic field before curing. The CTE in the parallel direction is very low, ranging from –17 to +8 in the parallel direction, closer to the carbon fiber CTE than any other resin in the table. The CTE in the perpendicular direction is high due to the presence of the methyl group on the aromatic ring, which is used to reduce the temperature of the nematic phase in order to cure with the electron beam at low temperature. The CTE of a resin without that methyl group would be reduced and the stiffness of such a cured resin would be greater. The Differential Scanning Calorimetry curve of the RM 257 is shown in Figure 3.



Liquid Crystal Resin RM 257

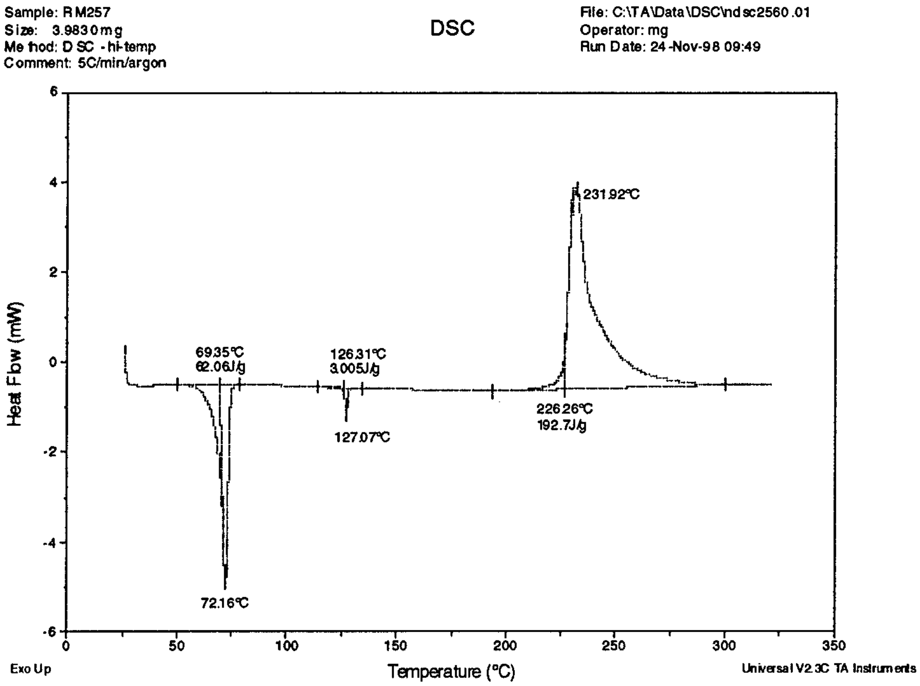


Figure 3. This DSC of commercially available RM 257(Merck) shows a transition from crystalline to liquid crystalline at 72°C and a transition to isotropic melt at 127°C. The transition at 231°C is due to thermal polymerization of the compound.

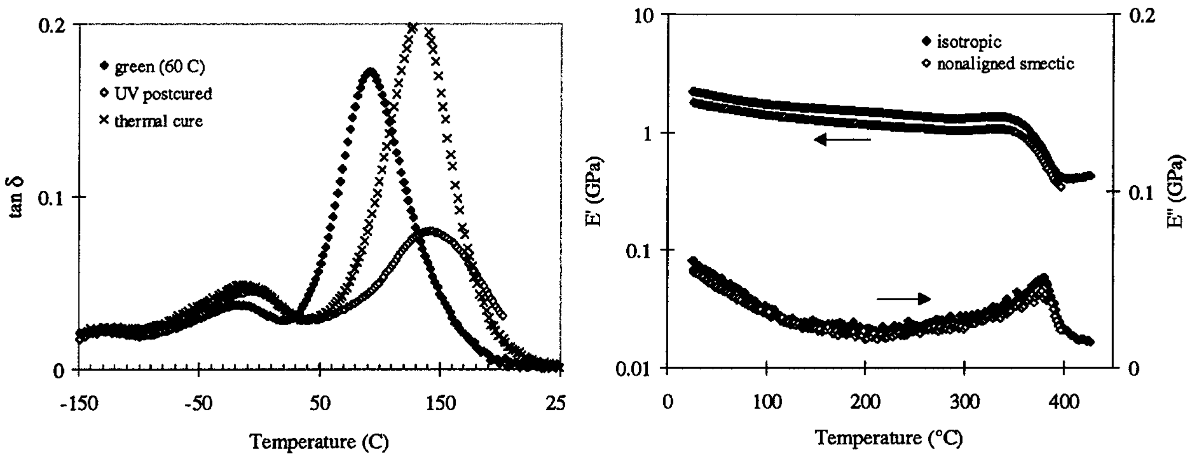


Figure 4. (left) Dynamic mechanical loss tangent data for an LC monomer cured by both UV and heat. UV cure was by single light exposure (green) at 60°C and second light exposure at 150°C. The thermal cure was at 150°C. The γ transition at about –140°C suggests that the cryogenic fracture resistance of the LC resins will be superior to many thermosets. (right) The dynamic mechanical spectrum of an LC that postcures by a thermal reaction after radiation curing shows modulus retention above 300°C and the T_g in excess of 300°C.

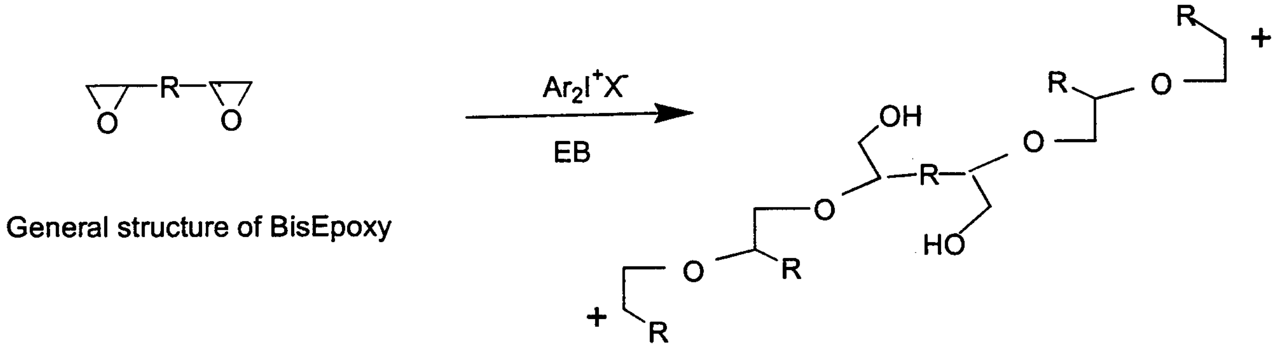


Figure 5. The cationic epoxy polymerization mechanism produces relatively few cross-link sites compared to conventional epoxy cure mechanisms. Cross-linking can be achieved only through the hydroxyl groups or by using multifunctional epoxies, which become more difficult to process as their functionality increases.

4.3.3 Cationic Epoxies

Several cationic epoxy resins formulated for cryogenic applications were supplied by Applied Poleramic. These formulations were supplied as films and were both primary and secondary phase toughened. They contained from 15 to 70% toughener. The results of characterization tests are described in the section on mechanical testing.

4.3.4 Nanoparticle Reinforced Resins

A base resin consisting of a mixture of difunctional epoxy acrylate and reactive diluent difunctional acrylate was stirred under high shear with 5 and 10 weight % monmorillinite clay. A coupling compound that formed an ionic bond with the clay and contains methacrylate groups for electron–beam–curing was added in a stoichiometric amount to the CloisiteNa (Southern Clay). The clay exfoliates during the high speed mixing and its reinforcing effect is maximized. The resins were electron–beam–cured and their flex strength was measured. The results are shown in Figure 6. Stiffening up to 100% can be achieved by modification of the clay surface treatment, modification of the coupling compound, or increase in the amount of added clay.

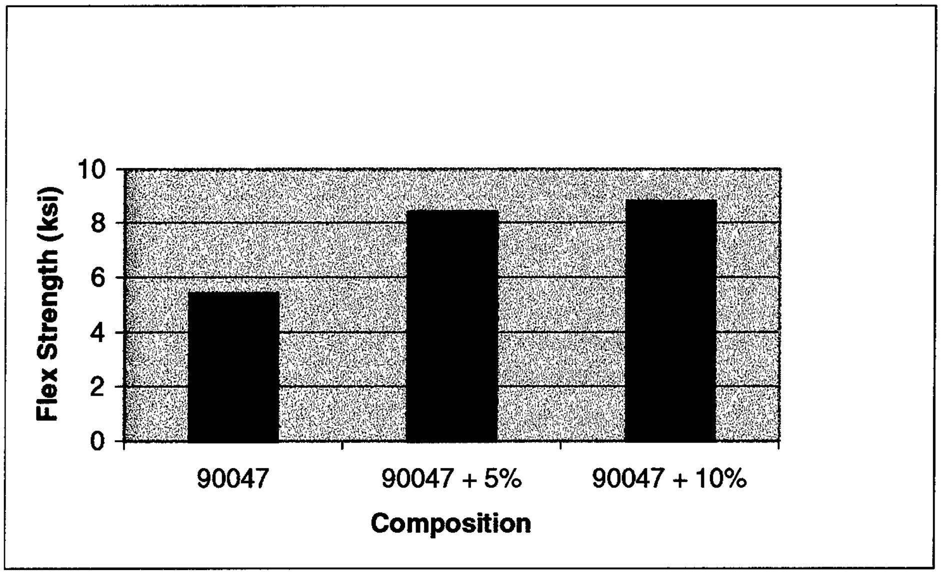


Figure 6. The Effect of Exfoliated Nanoclay on the Stiffness of Cured Acrylate Resin. The stiffness increased 65% in the 10% reinforced resin. X-ray examination indicates a high level of exfoliation with the 10% reinforcement. Additional clay can increase stiffness until crowding of the sheets of clay starts to reduce the effect. Many types of surface treated clay are available.

4.4 Mechanical Testing Results

Mechanical testing was performed on both cured resin plaques and on cured woven carbon fiber composites. Two unidirectional composites were also fabricated and tested.

4.4.1 Mechanical Testing Of Cured Resins

Mechanical testing of cured resin plaques was performed at room temperature and in liquid nitrogen. The results are shown in Table 5.

Table 5. The results of mechanical testing of cured resins.

Resin	Toughener (wt %)	Compact tension (psi in$^{1/2}$)	Flex Strength (ksi)	Flex Modulus (ksi)	Flex Strength (ksi) in LN_2	Flex Modulus (ksi) in LN_2
SRL1-90047/ 1-582	50	361±29	8.7±1.0	198±4.7	34.1±4.2	1165±27
SRL3-90047/ 1-582	25	325±45	14.9±0.5	399±8.9	24.0±3.3	1201±38
SRL EBA-1	15	993±106	9.0±0.6	308±1.9	11.1±1.8	930±30
SRL VCCM4	15	No data	18.6±1.0	560±35	No data	No data
Cytec Fiberite 977-2	proprietary	Not reported	28.6±1.0	500±10	Not reported	Not reported

The resin formulation that has been characterized to the greatest extent at room temperature is the SRLVCCM4, the dual curing resin characterized in untoughened form in previous programs, shown here in secondary phase toughened form. The SRL EBA-1 is a newly formulated cationic epoxy that is secondary phase toughened. The SRL 90047/582 single-phase mixtures are base resin/toughener mixtures that are not fully formulated. They were used in an attempt to start to learn the effects of increased toughener levels on properties at cryogenic temperatures. Compact tension results can be compared to a value of about 600psi in$^{1/2}$ for thermally cured epoxy resins and for LC in the unaligned nematic phase (RM 257) from EM Industries, Inc. and a value of about 300 psi in$^{1/2}$ in the cured isotropic state. The resins show increased flex strength and modulus in LN_2, as expected for potential cryogenic composites. The electron–beam–cured resins show about half to three-quarters of the flex strength of 977-2 at ambient temperature, with properties at cryogenic temperatures to be compared in future work.

4.4.2 Composite Testing Results

The results of tests on woven composites are shown in Table 6. The composites were prepared as follows. The KB-4, KB-3 and EBA-1 are all cationic epoxies. They were supplied as films that were assembled in alternating layers with the AS4 cloth so that a weight of 50% resin was achieved. The plies were vacuum bagged and heated to 100 to 110°C for consolidation before electron–beam–curing to a dose of 30 MR at ambient temperature in vacuum. The KB-4 is a single–phase resin and the other two formulations are secondary phase toughened. SRLVCCM4 is a secondary phase toughened dual curing epoxy acrylate that was prepared by VARTM, thermally cured at 50°C for six hours and then electron–beam–cured to a dose of 20 MR. The SRL 90047/582 resins are primary phase toughened base resins containing epoxy acrylate and reactive diluent. They are models for highly toughened free radical curing systems. They were prepared by wet lay-up, vacuum bagging at 80°C for consolidation and cured to a dose of 20 MR in vacuum.

Table 6. Mechanical Test results on composites prepared with 12K 5 HS AS4 woven cloth with G' sizing.

Composite Resin	Interlaminar Shear Strength (ksi)	Interlaminar Shear Strength (ksi) (–196°C)	Short Beam Shear Strength (ksi) after 5 cycles between 20°C and –196°
SRL VCCM4 dual cure two-phase (20% rubber)	6.4±0.3[1,3]	6.4±0.2[1]	No data
SRL KB-4 cationic epoxy one-phase (70 % rubber)	6.9±1.4[2]	No data	7.0[2]
SRL KB-3 cationic epoxy two-phase (30% rubber)	5.2±0.2[2]	No data	4.7±0.3[2]
SRL EBA-1 cationic epoxy two-phase	2.4±0.2[1]	2.1±0.2[1]	2.7±1.2[2]
SRL 3-90047/1-582 free radical one phase (25% rubber)	2.0±0.3[1]	2.6±0.4[1]	No data
SRL 1-90047/1-582 free radical one phase (50% rubber)	2.3±0.1[1]	3.1±0.2[1]	2.1±0.1[2]

[1] ASTM D2344 4-point loading

[2] ASTM D2344 3 point loading

[3] This composite contained significant voids. Previous results at ambient temperature indicate an ILSS of 8.8±0.2

Four composites were compared at ambient temperature and in LN_2. The results show retention of interlaminar shear strength (ILSS) in LN_2 and the highest results of about 6 to 7 ksi for the composite prepared with dual–curing resin and that prepared with a cationic epoxy containing a high level of toughener. The SRL 90047/582 composites both show 20 to 30% increased ILSS in LN_2, which suggests that primary phase toughening is better for cryogenic composite resins. A cured resin should be stiffer at a colder temperature, whereas no increase in stiffness suggests microcracking. Future efforts will be directed toward repeating and verifying these results with improved one-phase formulations and with combinations of primary and secondary phase tougheners.

Four composites were subjected to thermal cycling for 5 cycles in LN_2 prior to testing at ambient temperature. They all maintained ILSS values after cycling. The cycling was performed manually over fifteen to thirty minutes for each cycle to eliminate thermal shock. Microcracking was not visible in the cycled composites under the microscope. The samples were viewed without any polishing or imbedding to make microcracking more visible. This technique will be used in future research.

4.4.3 Void Content and Fiber Volume Fraction

The void content and fiber volume fractions for 4 composites are shown in Figure 7 and in Table 7. The SRLVCCM4 shows an acceptable fiber volume fraction of 53%, but the photomicrograph shows some voids that contributed to lower ILSS than has previously been measured for this system at ambient temperature. The other three composites show low fiber volume fractions due to resin viscosity issues and the fact that they were first used in this short program without optimization. The photomicrograph for SRL EBA-1 shows resin rich areas, while the SRL 90047/582 – based composites show poor fiber wetting in both and voids in the SRL 3-90047/1-582. These composite resin formulations were base resins for the dual–curing systems mixed with toughener used as models for primary phase resins. They were not fully formulated in Phase I, but single-phase dual–curing resins will be important candidates for testing in the Phase II program.

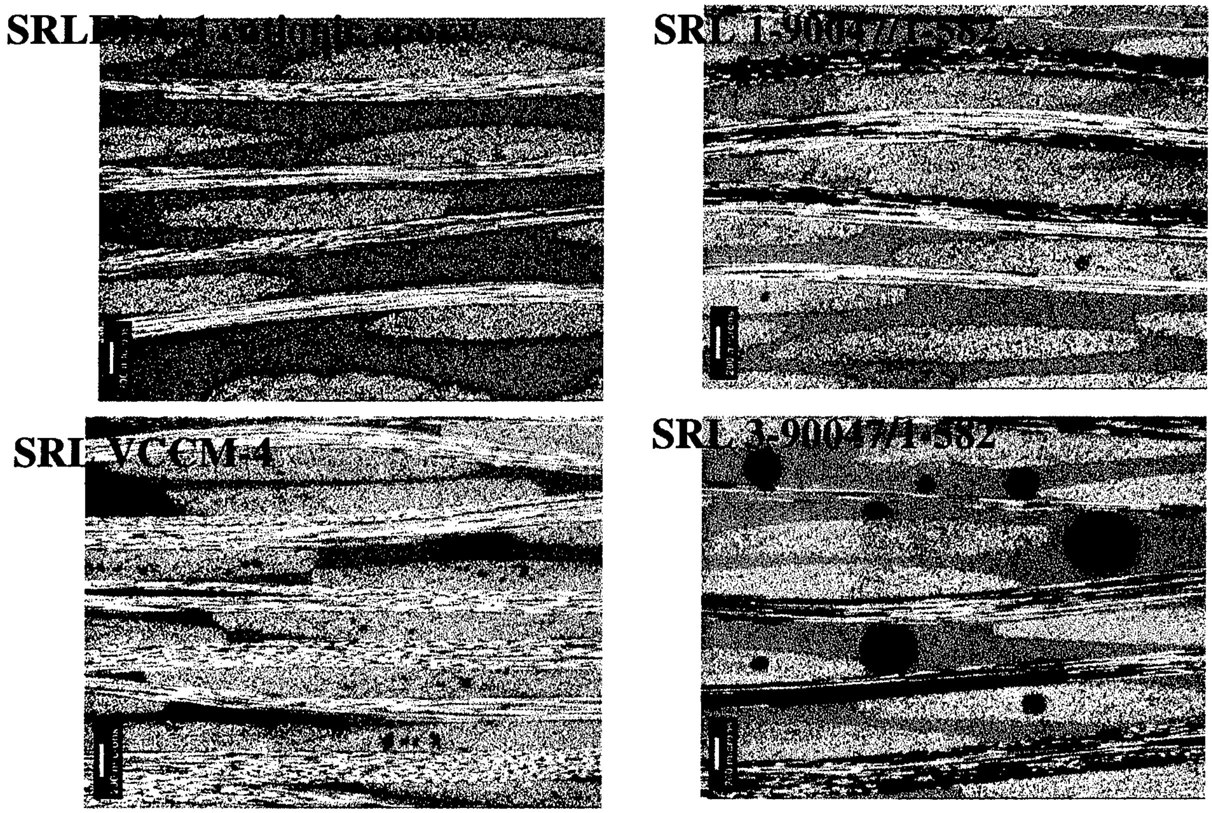


Figure 7. Photomicrographs of composites fabricated for mechanical testing at ambient temperature and in liquid nitrogen. SRLVCCM4 is a relatively well-developed resin prepared by VARTM, while the other three composites were prepared from model resin systems that were not optimized for viscosity. SRL EBA-1 was prepared from a film-forming resin. The two composites prepared from mixtures of epoxy acrylate base resin 90047 and urethane acrylate 582 toughener were high viscosity mixtures.

Table 7. The Fiber Volume Fraction and Void Content for the Principal Composites Tested.

Composite Panel AS4-5HS (G')	Resin Specific Gravity[1]	Resin Content (wt%)[2]	Fiber Volume Fraction (vol%)[2]	(vol%)[3]	Void Content (vol%)[2]
SRL EBA-1	1.134	50.6	38.1	39	<1
SRL 1-90047/1-582	1.149	57.3	31.4	32	2.5
SRL 3-90047/1-582	1.18	48.1	39.9	38	3.6
SRL VCCM-4	1.15[4]	35.4[5]	53.1[5]	53	1.5[5]

[1] Procedure: ASTM D792 (weight in air, weight in water)

[2] Procedure: ASTM D3171 (acid digestion)

[3] Calculated based upon panel thickness, number of plies, fiber aerial weight (g/cm^2) and fiber density (g/cm^2)

[4] resin plaque not available, value estimated

[5] based on estimated specific gravity

Table 8. Interlaminar shear strength of unidirectional composites prepared from 12K AS4 with a G' finish.

Unidirectional Composite sample 12K AS4 G'	Interlaminar Shear Strength at RT (ksi)	Interlaminar Shear Strength (ksi) at RT after 5 cycles between 20°C and –196°
SRL1-90047/1-582	2.1±0.2	2.1±0.3
SRL LC RM257	2.6±0.4	3.0±0.1

4.4.4 Unidirectional Liquid Crystal Composite

This is the first time that a unidirectional composite has been prepared from the Liquid Crystal compound. The SRL 1-90047/1-582 was prepared for comparison with the woven composites shown in Table 6. The ILSS for the SRL 1-90047/1-582 – based unidirectional composite is 2.1 ksi at room temperature and is within 10 % of the value for the woven composite shown in Table 6. The SRL LC RM257 – based composite shows comparable values at ambient temperature and after cycling in LN_2 for 5 cycles. The LC resins are new materials for composite materials and not much is known about them so far. Free radical curing LC resins for electron–beam–cured composites need to be investigated on a continuing basis because of their stiffness potential.

Another factor that has not been considered in Phase I is the compatibility of the fiber finish with the different resins, which contributes to the strength of the composite. Composite properties from materials using varied fiber finishes will be compared in the follow-on program.

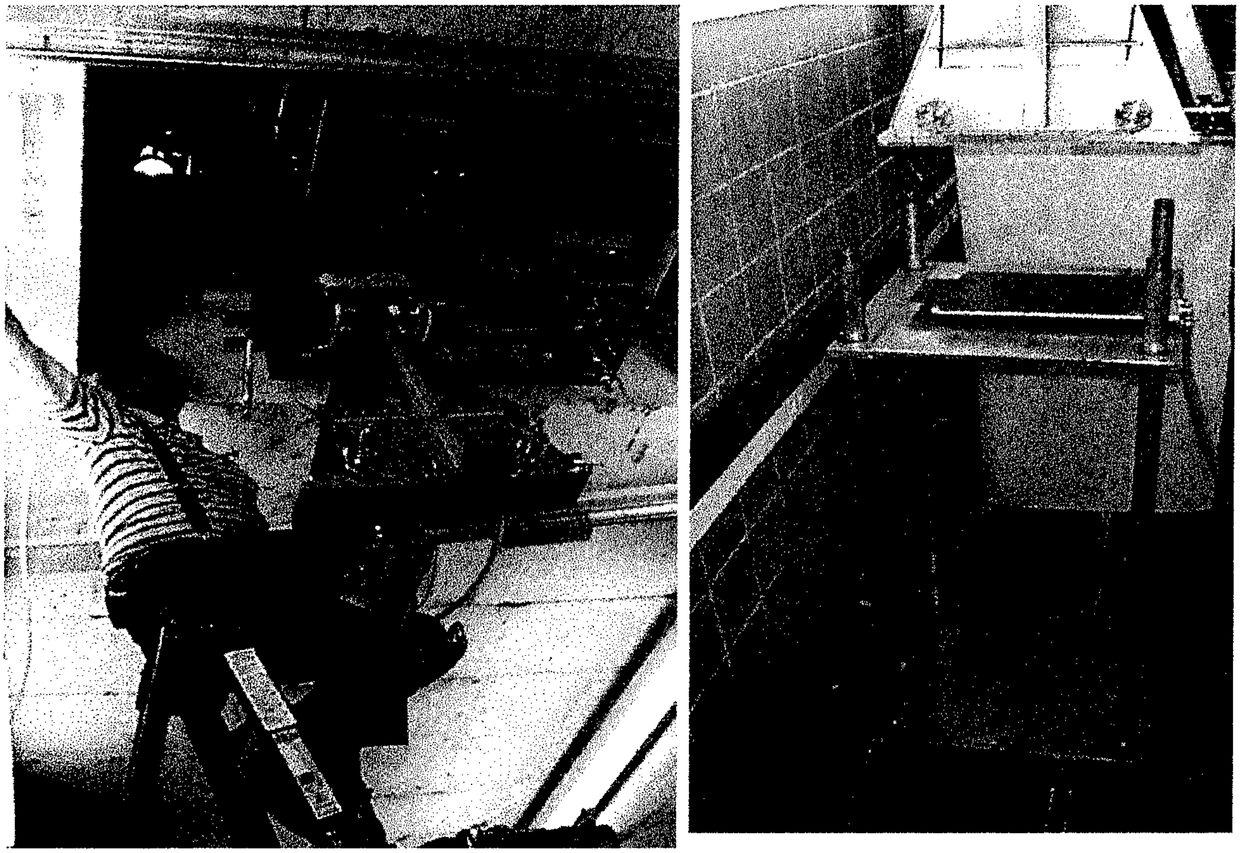


Figure 8. SRL's 4 MeV accelerator was used to cure all the resins and composites using the cart that travels back and forth under the scan horn, as the beam is scanned perpendicular to the cart travel direction.

4.4.5 The Effect of Temperature on Curing

4.4.5.1 Curing at Elevated Temperature

Electron–beam–curing can be performed over a wide range of temperatures. Most curing reactions start at room temperature and heat up during irradiation. A dose of 10 MR is the energy density needed to raise unit density material with the same specific heat as water about 20°C. The heat generated by the exothermic polymerization reaction is also added. Curing at a range of temperatures is of great value for liquid crystals, where curing in the nematic phase locks in the long-range order in the resin and maximizes the stiffness. The unidirectional composite shown in Table 8 was cured at 86°C in the nematic phase. The experimental setup is shown in Figure 9. The SRL LC RM257 and other electron–beam–curable LCs being developed at the University of Dayton Research Institute are designed to have a nematic phase at a relatively low temperature so that they can be cured in the electron beam without excessive heating. In order to achieve this, the methyl group was added to the aromatic ring in the compound, which results in a decrease in stiffness. Modification of the chemical structures is underway at UDRI to optimize both the crystalline to nematic transition temperature and the stiffness of the resins.

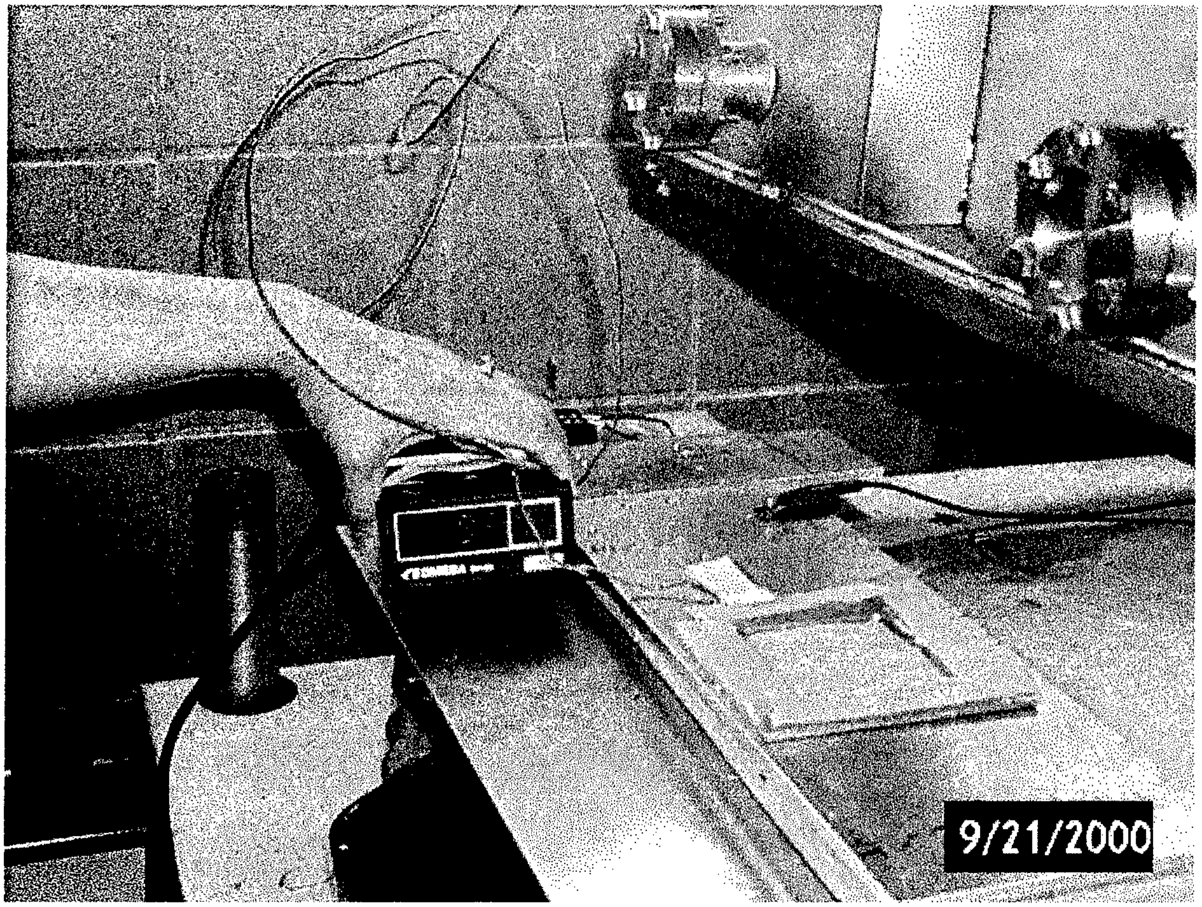

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Figure 9. The unidirectional LC composite heated to 86°C ready for curing in the electron beam.

4.4.5.2 Cryogenic Curing

An experiment to investigate the effect of cryogenic temperature on the effectiveness of curing in the electron beam is shown in Figure 10. It was difficult to cool the BR-582 (Bomar Specialties) urethane acrylate to –196°C without cracking it. Within about 20°C of the T_g of the uncured urethane (about –40°C), cracking was observed. Curing of the cracked resin occurred in the electron beam accompanied by a temperature increase to about –170°C and it exhibited a T_g of –22°C by DSC. Another resin, epoxy acrylate CN 104 from Sartomer Co., which probably has a higher T_g in the uncured state than BR 582, did not cure in LN_2.

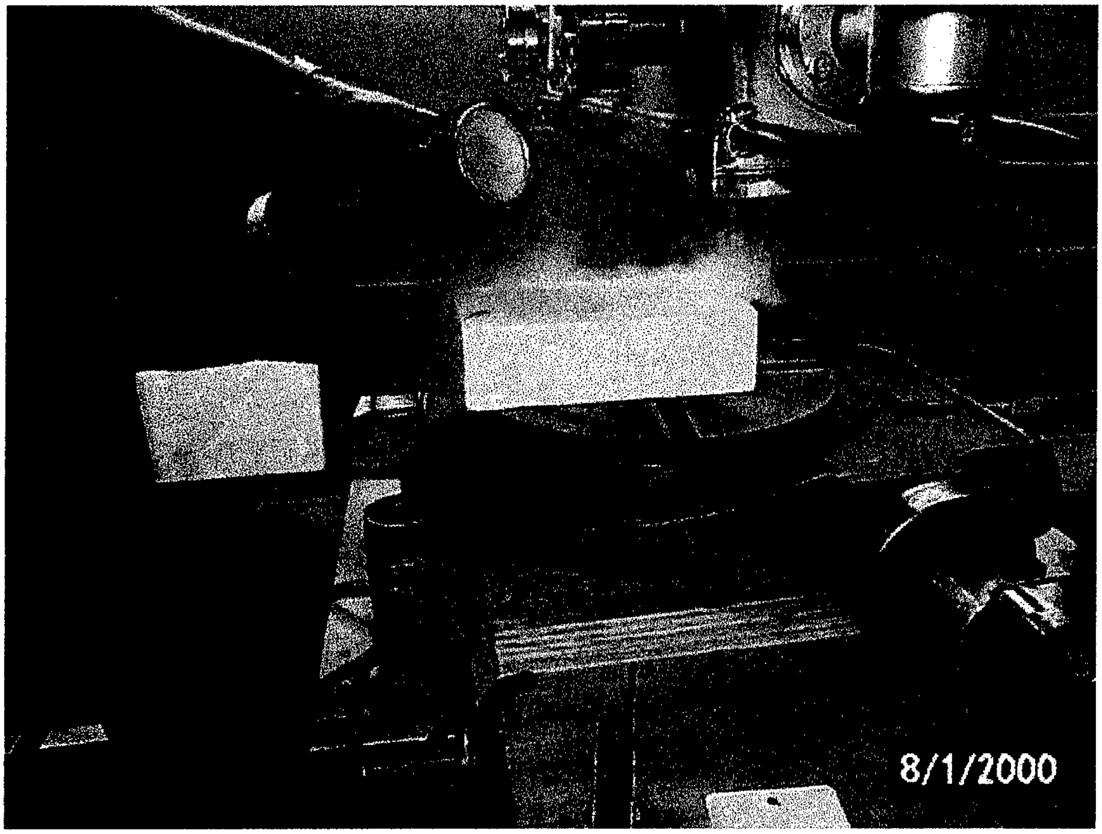

Figure 10. A urethane acrylate with an uncured T_g of about –40°C is cooled to –196°C before curing under the scan horn of the electron accelerator. The resin cured at that temperature by a free radical mechanism, but showed cracks that occurred as it cooled down within 20°C of the T_g. Slow programmed cooling to selected cold temperatures will eliminate the cracking that occurs before electron–beam–curing.

5. CONCLUSIONS AND FUTURE RESEARCH

Even though the composite properties are rather low for the materials studied in Phase I, the fact that the properties do not decline in liquid nitrogen indicates that reformulation of the resins for improved processing and improved mechanical properties at ambient and at cryogenic temperature is a promising approach for Phase II. Non-autoclave EB-curing of large composite structures is a promising approach for fabrication of SOV cryotanks and other space structures too large for existing autoclaves.

5.1 EB–Curable Resin Development And Composite Fabrication

The Phase II program will include extending the use of tougheners in free radical and cationic resins, including both secondary and primary phase tougheners, newer materials as they become available and varied weight % of tougheners for cryogenic applications. Formulation using trifunctional epoxy acrylate will result in an increase in the T_g of the dual–curing resin system. The dual–curing (thermal/EB) SRLVCCM4 resin will be reformulated into a fully EB–curable resin by replacing the thermally cured epoxy–amine with pre–polymerized adducts that mix in the resin before electron–beam–curing. Nanoparticle stiffening will be optimized with clay surface treatment and coupling compounds. Carbon nanotubes can also be used to stiffen the electron–beam–curable resins and composites. Epoxy acrylate and liquid crystal towpreg and unidirectional prepregs will be prepared and fabricated into composites.

The resins and composites will be tested at room temperature and in liquid nitrogen. For the resins, mechanical testing will include tensile strength, tensile modulus and strain to failure and compact tension at both temperatures. For the composites, coordination with the Air Force Research Laboratory and the Non-Autoclave Materials for Large Composite Structures contractors at Boeing will be required. Composite testing will include 0°, ±45°, 90° tension, double cantilever beam (ASTM D5528-94A), end notched flexure (ASTM D 30.02 Round Robin) and microcrack density/first ply failure in [0/90/0] composites. Thermal and mechanical testing of quasi-isotropic laminates in liquid hydrogen will be coordinated with testing at Boeing.

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