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Electron Beam (EB) curing of resin and adhesive offers significant advantages for fabricating and bonding of fiber-reinforced polymer composites for ground vehicle structural components. The EB curing process reduces the time to cross-link the polymer matrix or the adhesive compared to conventional heat curing. The process allows curing at room temperature for high throughput and reduced residual stresses for good part fit-up. EB adhesive curing also prevents de-bonding of dissimilar materials that can occur during the cool-down cycle. As part of this SBIR, Science Research Laboratory (SRL) has developed resins, adhesives and electron gun technology for high-energy electron beam curing and bonding of composites. During Phase I, SRL developed B-stageable, EB-curable resins suitable for a high for the resin transfer molding / electron beam curing process. SRL also developed a costing model for this process and applied the model to one high-quantity part. During Phase II, SRL optimized and tested the novel resin system, and used the resins in production of EB-cured panels for the Army's Composite Armored Vehicle. SRL also developed novel EB-curable adhesives and demonstrated the advantages of EB curing of adhesives for automotive applications by bonding together test panels of the Chrysler Composite Concept Vehicle. Commercialization of EB curing in the automotive industry is continuing as part of SRL collaborations with Daimler-Chrysler and Ford. Because the properties of the B-stageable EB-curable resins were better than expected, and because of the processing advantages of B-staging, the aerospace community is also considering the use of these resins for aircraft parts. Resin and adhesive samples and associated design data have been requested by two groups at Boeing, and by designers at Lockheed Martin, Northrop Grumman and Raytheon/Hughes.

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WITH HIGH ENERGY ELECTRON BEAMS

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WITH HIGH ENERGY ELECTRON BEAMS

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ADVANCED LOW-COST COMPOSITE CURING
WITH HIGH ENERGY ELECTRON BEAMS

Abstract

Electron Beam (EB) curing of resin and adhesive offers significant advantages for fabricating and bonding of fiber-reinforced polymer composites for ground vehicle structural components. The EB curing process reduces the time to cross-link the polymer matrix or the adhesive compared to conventional heat curing. The process allows curing at room temperature for high throughput and reduced residual stresses for good part fit-up. EB adhesive curing also prevents de-bonding of dissimilar materials that can occur during the cool-down cycle.

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Section 1. Introduction

This purpose of this SBIR program was to develop electron beam curable materials and processes appropriate for ground vehicles and to demonstrate these materials and processes by fabricating military and commercial vehicle parts. All

program goals were met. Novel resins and adhesives with processing advantages were developed. Parts for the Army Composite Armored Vehicle and the Chrysler Composite Concept Vehicle were fabricated. The properties of these novel resins sufficiently exceeded the baseline heat-curable systems that the aerospace community is interested in using the materials for aircraft applications. Daimler-Chrysler Corporation is also interested in bonding composite vehicles using the electron beam process.

1.1 Executive Summary

- Novel Processes and Materials Developed for Electron Beam Curing of Composites
    - "Tool-Free" resins react to handleable B-staged solid prior to EB cure.
    - Low cure shrinkage from interpenetrating network for reduced residual stresses.
    - All thermal and mechanical properties exceed vinyl ester baseline.
    - US Patent protection applied for, and recently received for the "Tool-Free" EB cure process and materials.
- Novel Adhesives Developed for Bonding of Automotive Parts
    - Room temperature "command cure" adhesive bonds materials with dissimilar thermal expansion (i.e. composite to steel) without residual stresses.
    - Dual EB/Room Temp curing adhesive meet Chrysler cost and property targets.
- Cost modeling shows process advantages for ground vehicles.
    - Resin transfer molding followed by EB cure for high rate production of automotive parts.
    - RTM/EB cure is cost effective at moderate production quantities.
    - Bonding of composites and steel in two-minute cycle times without heating.
- Demonstration Composite Parts Fabricated and Bonded
    - Army Composite Armored Vehicle (CAV) parts
    - Chrysler Composite Concept Vehicle (CCV) parts
- CAV Parts Demonstrate Thick Section EB Curing
    - Multiple materials cured and bonded, including ceramic armor, rubber and 1-inch thick composite laminate.
    - Room temperature VARTM with B-stageable resins.
    - Ballistic testing of stitched and unstitched panels matches thermally cured specs.

- CCV Test Panels Demonstrate Automotive EB Bonding
  - Joining of thermoplastic composite without melting.
  - Coupon and medium-scale test panels meet Chrysler specifications.
  - Joining of CCV inner-outer side panels and frame begun as a commercial Phase III follow-on to this Phase II program.

1.2   Background and Motivation

The use of composites in military and commercial ground vehicles continues to increase. Two good examples of this trend are the Army's Composite Armored Vehicle (CAV) [1] and Chrysler's Composite Concept Vehicle [2], both composed primarily of glass reinforced composites. The advantages of using composites are well known, and include high strength-to-weight ratios, corrosion resistant and low weight.

There are several molding and bonding processes used to manufacture ground vehicle containing composites. These conventional techniques all incorporate a heat-curing step to cross-link the polymer matrix or the adhesive, converting the resin or adhesive from a viscous liquid to a stable solid. Heat curing is a slow process and has other disadvantages including the release of volatile organic vapors and creation of residual mechanical stresses, especially when combining materials with different thermal expansion coefficients.

High energy electron beam (EB) curing and bonding of polymer matrix composites do not have these limitations. EB curing is capable of much higher throughputs than heating for both fabrication and bonding. The majority of work to date in the area of electron beam curing of composites has been to develop materials that can meet the demanding mechanical properties and use temperatures required of aerospace parts [3].

The processes and materials described in this final report have the mechanical and thermal properties as well as the low cost to be useful for ground vehicle fabrication. One process that allows low cost and high throughput combines resin transfer molding (RTM) with EB cure. This process is described below in Section 1.3. Although this process was demonstrated in this program and has significant advantages, it represents a large (and

risky) step for a manufacturer. We believe that the first electron beam process that will be used commercially is for bonding using EB-curable adhesives. This process is described below in Section 1.4.

Prior to this effort, Science Research Laboratory (SRL) had developed a new generation of pulsed linear electron accelerators capable of cost efficient production of high average power beams for curing of vehicle composites. Based on the success of this SBIR program, SRL has spun off a company (Electron Solutions, Inc.) to sell the equipment and materials described herein. ESI has several customers who are building or testing prototype parts using this EB technology. See References [4-5] for a description of SRL high power linear induction accelerator technology and see the ESI web site at the address of Ref. [6] for more information on the availability of EB curing equipment and materials (including some developed under this SBIR program).

This report divided into 5 sections. Section 2. describes novel EB curable materials developed under this program including B-stageable resins (in subsection 2.1) and dual EB / Room Temperature curing adhesives for ground vehicle applications (in subsection 2.2). Sections 3 and 4 describe the use of these novel materials for two applications. Section 3 describes fabrication of composite armored panels for the Army's Composite Armored Vehicle (CAV). Section 4 describes the bonding of Chrysler's Composite Concept Vehicle (CCV). Conclusions and recommendations for future work are described in Section 5.

1.3 The RTM/EB Cure Process

Electron beam curing is a line-of-sight process where the uncured resin is exposed to the electron beam either directly or through tooling material such as a vacuum bag or a thin mold window. Direct curing without tooling obstacles ("Tool-free" curing) allows the electron beam to cure edges and corners without blockage. It is an efficient use of the beam since energy is deposited only in the composite, and not into the tool. Direct access also permits curing from both sides of the composite, more than doubling the allowed composite thickness. However, Tool-free curing requires that the uncured composite be a structurally sound, handleable solid, either partially cured to B-stage or solidified to a

crystalline or amorphous state. This approach for automotive applications was suggested by C. Billiu at Ticom [7] and is currently under investigation for aerospace applications. The concept is shown in Figures 1-3, and a schematic of the SNOMAD-IV induction accelerator EB curing system used in this program is shown in Figure 4.
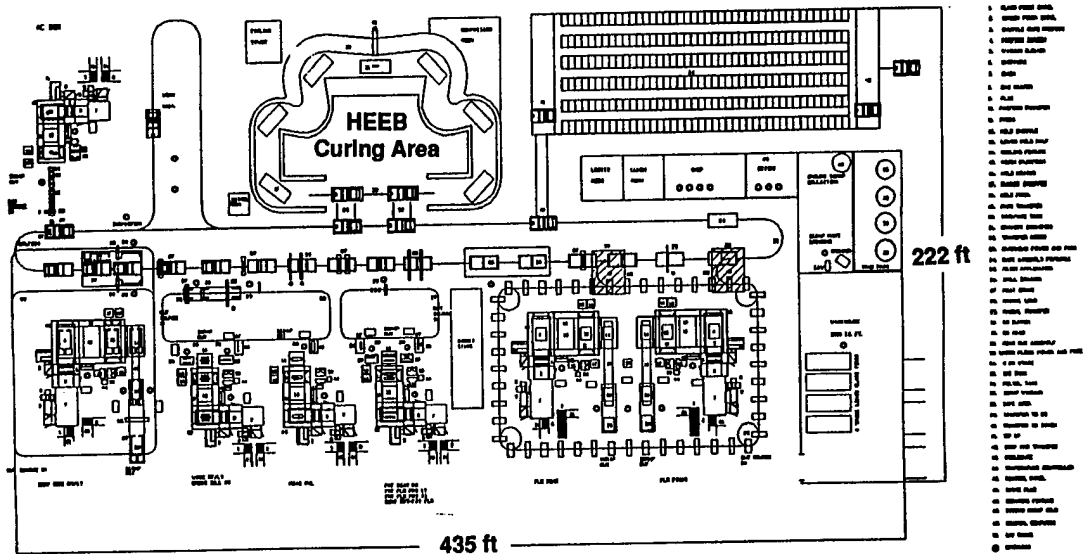
Figure 1: Layout of an automotive production plant combining RTM and EB cure. Completed cars ready for shipment are shown at the top right next to the EB area.
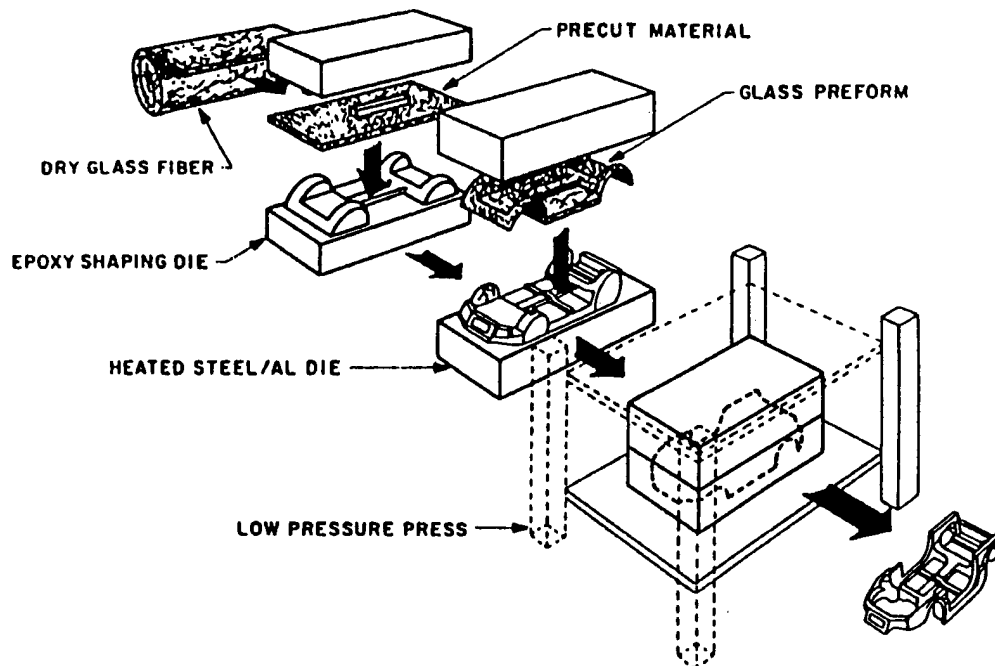
Figure 2: The RTM process for making vehicle parts.
After removal from the mold, the B-staged parts are cured and bonded using EB.

There are several variations on the RTM/EB Tool-free process, depending on application. For high throughput automotive parts, a preform of oriented glass fibers (chopped roving) is mixed with binder and shaped in a preform machine. The preform is transferred to a low pressure, heated press mold. A two-component reactive resin is injected and solidifies in place. After the composite is removed from the mold, it is ready for electron beam curing. For parts requiring higher stiffness (modulus), the process is similar. Continuous woven-roving reinforcement (rather than chopped fiber) is placed in the RTM mold. This process is slower and less amenable to complete automation than processes using chopped roving.

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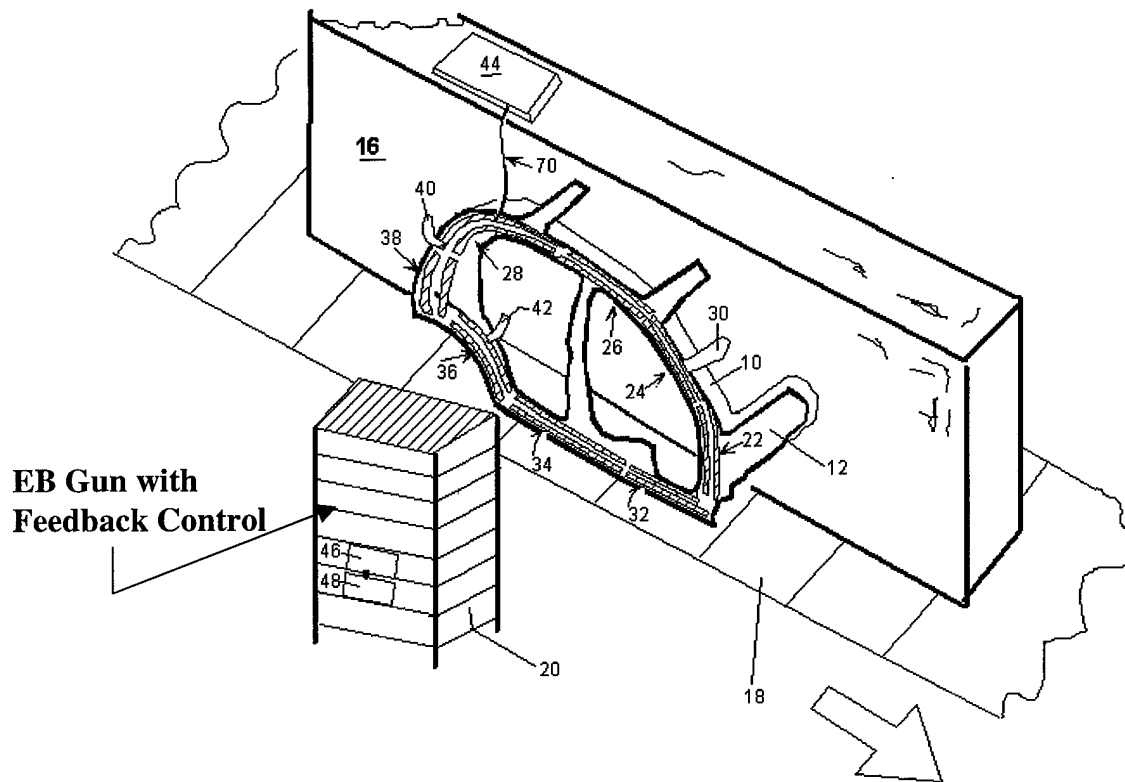
Figure 3: A system to bonding automotive components using EB curing.

If an appropriate two-component resin such as a system containing a polyisocyanate (or amine) + a catalyzed polyol is used in the RTM process, the result is a thermoplastic which can be cured by EB into a hard thermoset. The advantage of this technique is the ability to thermally "tack-weld" multiple composite parts together, adding an electron-beam-curable adhesive between the seams. It is even possible to add an acrylated paint, and then cure the frame, adhesive and paint together at one time.

A spread-sheet-based process costing model was developed during Phase 1 and extended during Phase 2 to determine the breakdown of costs for composites fabricated using this RTM/EB Tool-free curing process. This model determines the costs all the materials and processes required for part fabrication. For the RTM/EB Tool-Free system, processes include: fiber mat cutting, preform and core molding, preform assembly, resin transfer molding, electron beam curing and inspection. Raw materials include fibers, resins, mats, and catalysts.
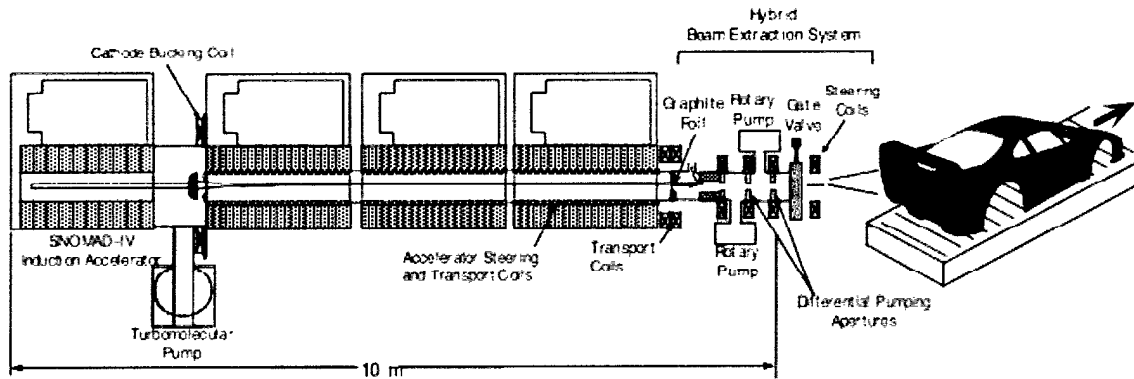
Figure 4: A schematic of the SNOMAD-IV EB composite curing system.

The inputs to the model are:

- Part specifications: size, weight, and production quantity.

- Material Choices: resins, catalysts, reinforcement fiber mats, cores.

- Equipment Choices: accelerator, tooling, presses.

- Accounting Model: Dedicated or nondedicated production lines.

- External Cost Factors: wages, electricity, repair and downtime, capital
  recovery rate.

The database in the model currently data for free radical and cationic EB-curable resins, six types of tooling, 20 electron guns from nine manufacturers and two part-handling systems. For each process, the model calculates:

- Variable Costs: Equipment cost, tooling cost, building cost, overhead labor cost,
  part cost ($)

- Installation cost, auxiliary equipment cost, maintenance cost, and capital cost
  (cost of money).

- Fixed Costs: Materials cost, labor cost and energy cost.

Results of the model are shown in Figure 5 and Figure 6. A 70 lb. automotive floorpan with a large existing costing model database was selected for cost modeling. Results are shown using the costs and performance of the SRL SNOMAD-IV. Figure 5(a) shows the per-unit production cost for this part as a function of yearly production quantity. For quantities of fewer than 150,000 per year, the RTM/EB Tool-Free process cost is lower than the steel stamping cost (including assembly).

From Figure 5(a), it can be seen that a large portion of the cost of components fabricated with conventional steel methods is due to the cost of assembly. By making large composites in the RTM/EB process, these costs are considerably reduced. Note that the RTM/EB per-unit cost remains constant over a wide range of production quantity. This is because tooling and presses for the RTM/EB process is inexpensive compared with steel stamping, and because these production quantities fully utilize the electron beam curing facility.

The "blip" in the steel stamping plus assembly cost is due to the need to add a second assembly line at production quantities over 250,000 per year. In reality, a manufacturer would probably save money by operating a third shift (overtime) to save the cost of installing a second line.

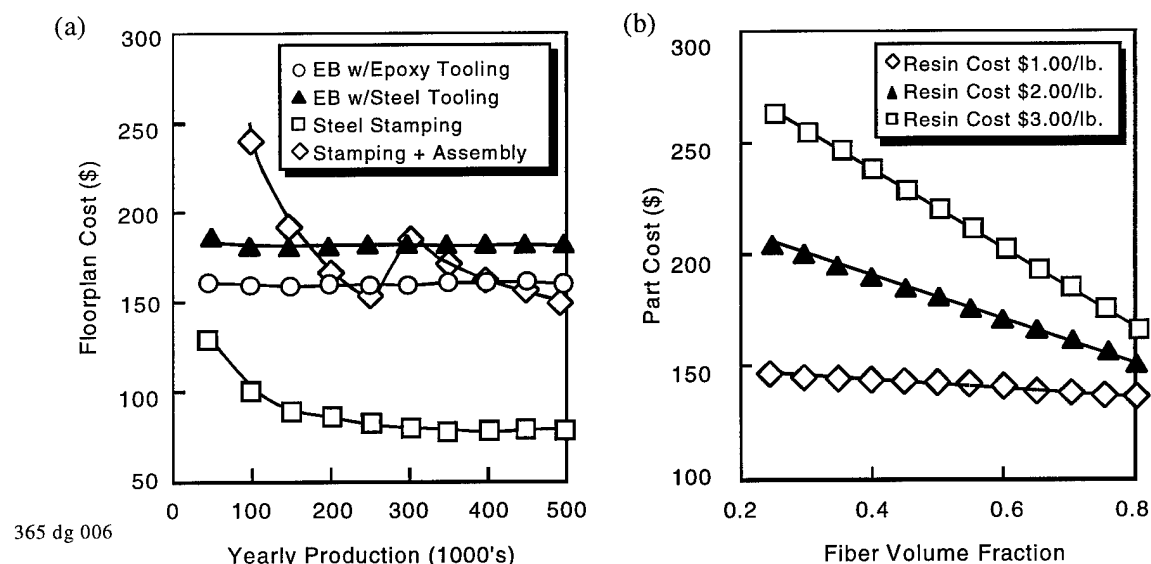Figure 5: Cost modeling for an automotive floorpan fabricated with EB cure.

Figure 5(b) shows the effect of fiber volume fraction and resin price on part cost. Fiber volume fractions for these components are typically in the 50-65% range. Present low quantity resin prices are between $2-$3/lb., giving a part cost of ~$200. Figure 5(b) shows that resin price is the most important cost driver for the overall part cost.
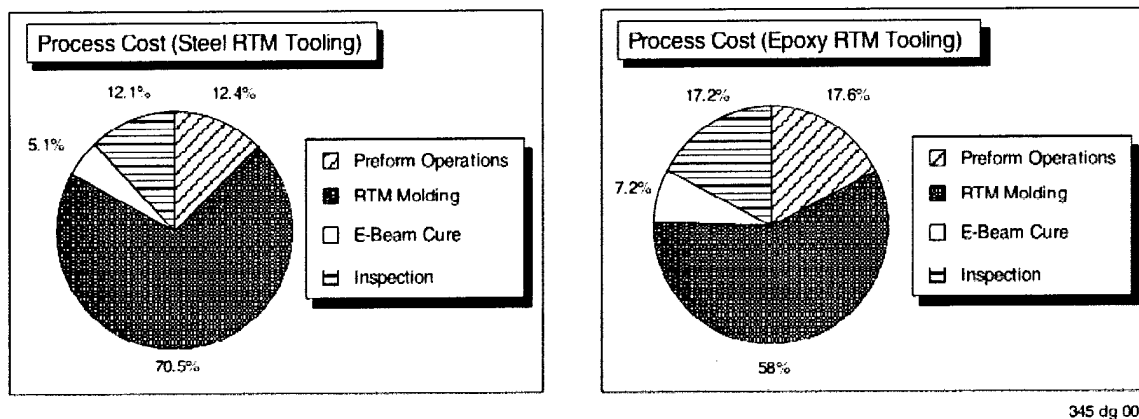
Figure 6: Cost breakdown for automotive floorpan fabricated by RTM/EB cure.

Figure 6 shows the relative cost of each RTM/EB process. Resin transfer molding constitutes the largest cost fraction (60-70%). The electron beam curing portion is a small fraction of the total process cost (5-7%). These figures also show that substantial reductions in process cost can be achieved if low cost epoxy tooling can be used instead of conventional steel tooling.

1.4 The EB-Bond Process

Although the amount of composite in automotive structural applications is still very small compared with steel, that fraction is expected to increase as manufacturers look for ways to save weight and reduce production costs. For example, Chrysler Corporation has displayed several all-plastic composite body prototypes at recent auto shows, and Chrysler executives have made public statements that they are considering production of such a vehicle [8]. They are also considering bonding together several other models using adhesives. These cars (and one from Ford that also will have significant amounts of adhesive) are shown in Figure 7.

Unlike conventional steel body cars, which are tack-welded together, plastic vehicles are bonded together with adhesive. SRL has been working with Chrysler for the past year, comparing heat-cured and electron beam cured adhesives for the Composite Concept Vehicle (CCV) and developing novel adhesives and EB curing equipment. The CCV body is composed of six large injection-molded pieces made of glass-reinforced

polyethylene terephthalate (PET). The car is shown in Figure 8 andFigure 9(b) and the inner- and outer- side body panels (before adhesive bonding) are shown in Figure 9(a).
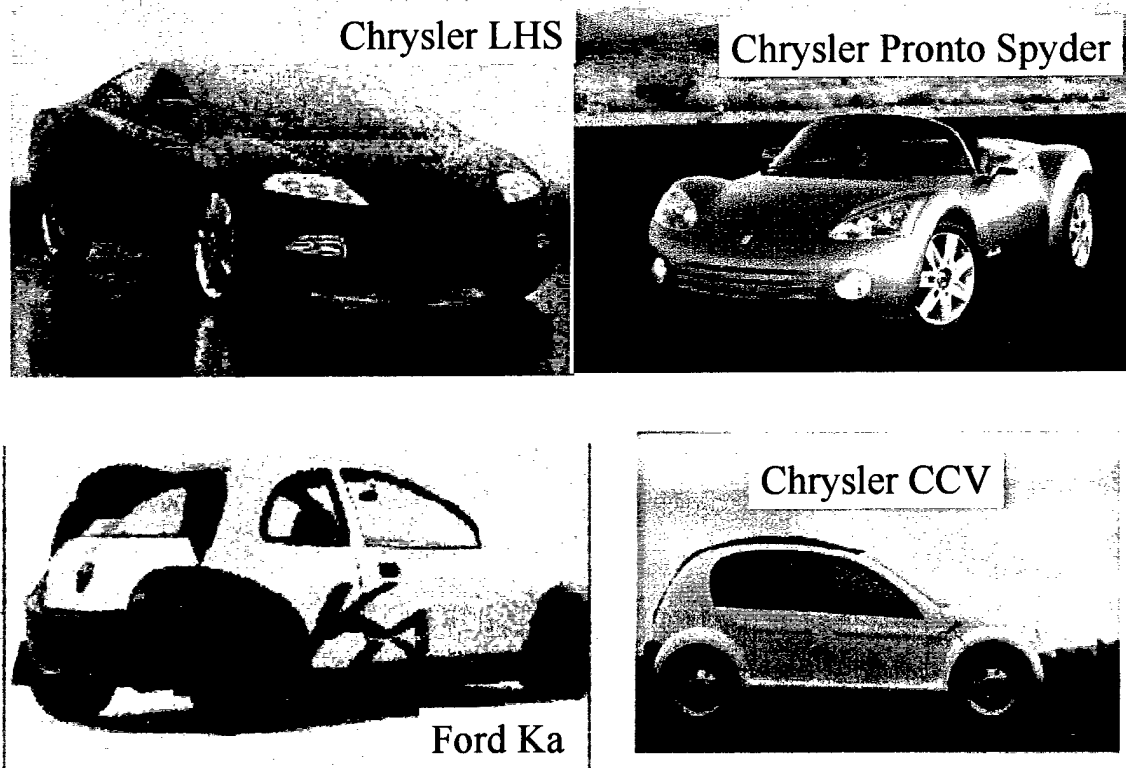

Figure 7: Automakers plan to use adhesive bonding to fabricate these models. The default is conventional heat curing, but Chrysler and Ford have expressed interest in using electron beam curing to decrease cycle time and prevent cracking due to thermal expansion mismatch.
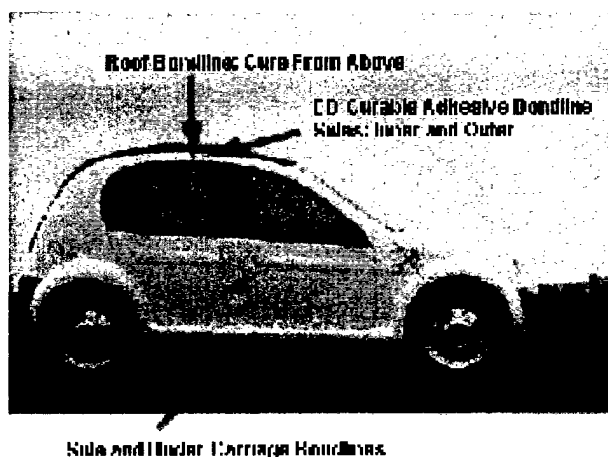
Figure 8: The Chrysler CCV showing bondlines for EB curable adhesive.
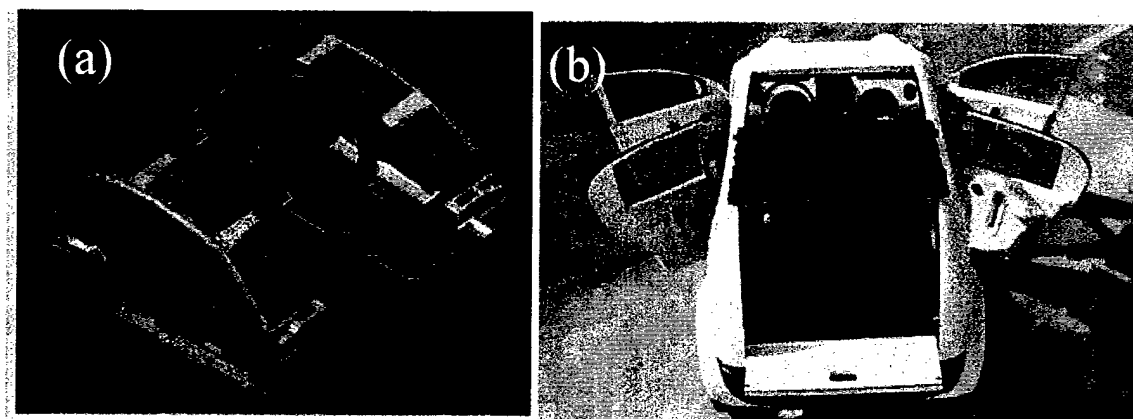
Figure 9: The Chrysler CCV is the first vehicle made of molded thermoplastic. (a) Inner and outer side panels, (b) rear view details including the fold-up roof and a left- or right-mounted steering column.

Section 2. Novel EB Curable Materials

2.1 "Tool-Free" B-stageable Resins

Although there are a number of processing methods that can be used to cure composites with radiation, they can be divided into two general categories: Curing while the resin matrix is in a liquid state or in a solid state. To cure a composite while the matrix is in a liquid state, the assembly must be enclosed in a mold, which determines the composite's final shape after it is cross-linked to a solid. Electron beams penetrate into the mold to crosslink the liquid resin matrix.

Alternatively, one may produce a handleable solid whose properties are improved by subsequent radiation cross-linking. This self-supporting solid is referred to as a ``green body'' at the process "B-stage." In this report, curing while the resin matrix is in a solid state will be designated as "free-standing" or "tool-free" curing, because no mold is required during the radiation curing process.

There are a number of processing and cost advantages to free-standing curing. Reference [7] describes how free-standing curing can be used to assemble a hollow section assembly. The cost advantages of using free-standing curing instead of conventional steel stamping at moderate production quantities are described in Section 1.2.

A generic problem in fabricating large structural composite parts is the difficulties of part fit-up. In applications involving the assembly of multiple parts, such as the case in automotive or aircraft applications, good part fit-up is necessary to allow final assembly, as well as for aerodynamic and aesthetic reasons. Unlike ductile metals, whose final shape can be modified by mechanical means at the final stages of assembly, rigid polymer matrix composites must achieve part fit-up by maintaining accurate fabrication tolerances.

In conventional composite processing (such as autoclave curing of aircraft composites), part fit-up problems are primarily caused by residual thermal stresses due to thermal expansion mismatch between fiber reinforcement and resin matrix upon cooling. A major advantage of low-temperature curing processes such as electron beam curing is the reduction in residual thermal stresses. However radiation curing has an analogous problem: resin shrinkage during cure. In composites, resin shrinkage leads to internal stresses, which can cause warpage of the composite part and poor part fit-up. It also leads to higher process engineering costs, since molds must be oversized or odd-shaped to account for shrinkage and warpage. In coatings, resin shrinkage can contribute to poor adhesion, especially to some metal substrates.

Conventional resin systems used in radiation curing shrink significantly when cured. Volumetric shrinkage values for common acrylic monomers are given in Ref. [9] and range from 11-30%.

Linear shrinkage of acrylated oligomers are listed in Ref. [10] and correspond to volumetric shrinkages of 7-25%. A typical resin formulation, incorporating such oligomers and monomers, will have a volumetric shrinkage of 9-15%.

One possible approach to reducing shrinkage of radiation-curable resins is the use of cationic polymerization [11] via cationic initiators possessing highly non-nucleophilic anions (PF_6^-, AsF_6^-, SbF_6^-). These are an alternative to the more common radiation-curable resin systems of the free-radical type, which possess carbon-to-carbon double bonds that cross-link upon exposure to radiation.

Radiation-induced cationic polymerization has shown lower shrinkage than free-radical systems (typically ~6% shrinkage). Cationic catalysts are, however, easily poisoned by nucleophilic resin components, contaminants or fiber sizings, making

radiation curing via cationic mechanism difficult. This is especially true for free-standing curing, where the presence of weakly nucleophilic urethane groups or of highly nucleophilic resin components such as amines are incompatible with the use of cationic catalysts. This problem is clearly illustrated by the entries in Table 1, which show that even slightly nucleophilic bonds such as found in N-phenylbutyramide or N-Butanol are sufficient to poison cationic polymerization.
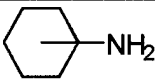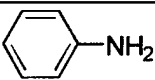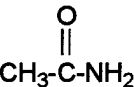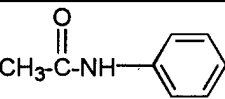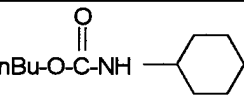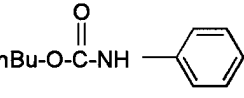
Additive (1.0 M)	pK_{BH+}	Curing of Vinyl Ether	Curing of Epoxy
(cyclohexyl)-NH$_2$	10.8	No	No
(phenyl)-NH$_2$	4.6	No	No
CH$_3$-C(=O)-NH$_2$	-0.5	No	No
CH$_3$-C(=O)-NH-(phenyl)	-1.0	Yes	No
nBu-O-C(=O)-NH-(cyclohexyl)	-1.2	Yes	No
nBu-O-C(=O)-NH-(phenyl)	-1.2	Yes	No
nBuOH	-2.0	Yes	Yes (chain transfer)
CH$_3$CN	-4.3	Yes	Yes

Table 1: Nucleophilic materials inhibit cationic polymerization.
We react nucleophilic amines and isocyanates with epoxies and hydroxy-containing compounds to achieve B-stage, and then use free-radical polymerization to cure carbon double bonds with EB. Data is taken from SRL experiments and from Ref [12].

In addition to the requirement for vehicles, the aerospace community also is looking for B-stageable EB-curable resins. Their proposed processing methods, such as shown in Figure 10, as well as the data in Table 1 shows that a method is needed for

formulating radiation-curable resins with low shrinkage for use in electron beam composite curing and coating applications, to achieve a free-standing "Tool-free" radiation cure.
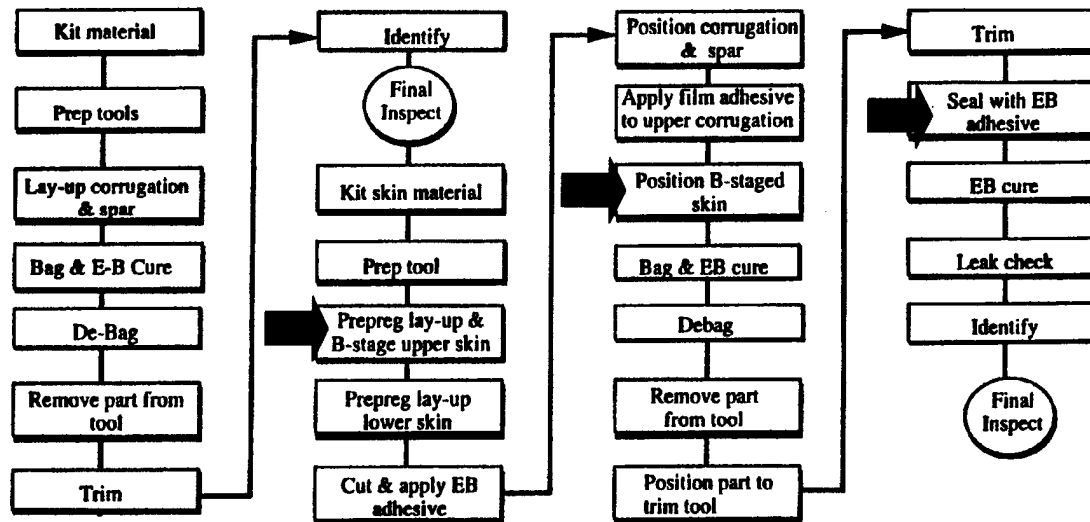
Figure 10: Aircraft component process flow using B-staging and EB curing.

As part of the DARPA-sponsored APCS program, Northrop-Grumman found that B-staging is the lowest cost approach to using EB-curable systems, capable of reducing processing costs by up to 65%.

The chemistry of two such systems are shown in Figure 11. Both utilize two-component meter mixed resins, which react at or near room temperature to form a handleable solid. For the urethane system shown in Figure 11(a), the "A" side contains a multifunctional isocyanate similar to the Dow PAPI 2000 series. The "B" side is a mixture of acrylated diluent monomers and oligomers. A typical oligomer contains an acrylated epoxies such as bisphenol-A epoxy dimethacrylate (commonly known as bis-GMA).
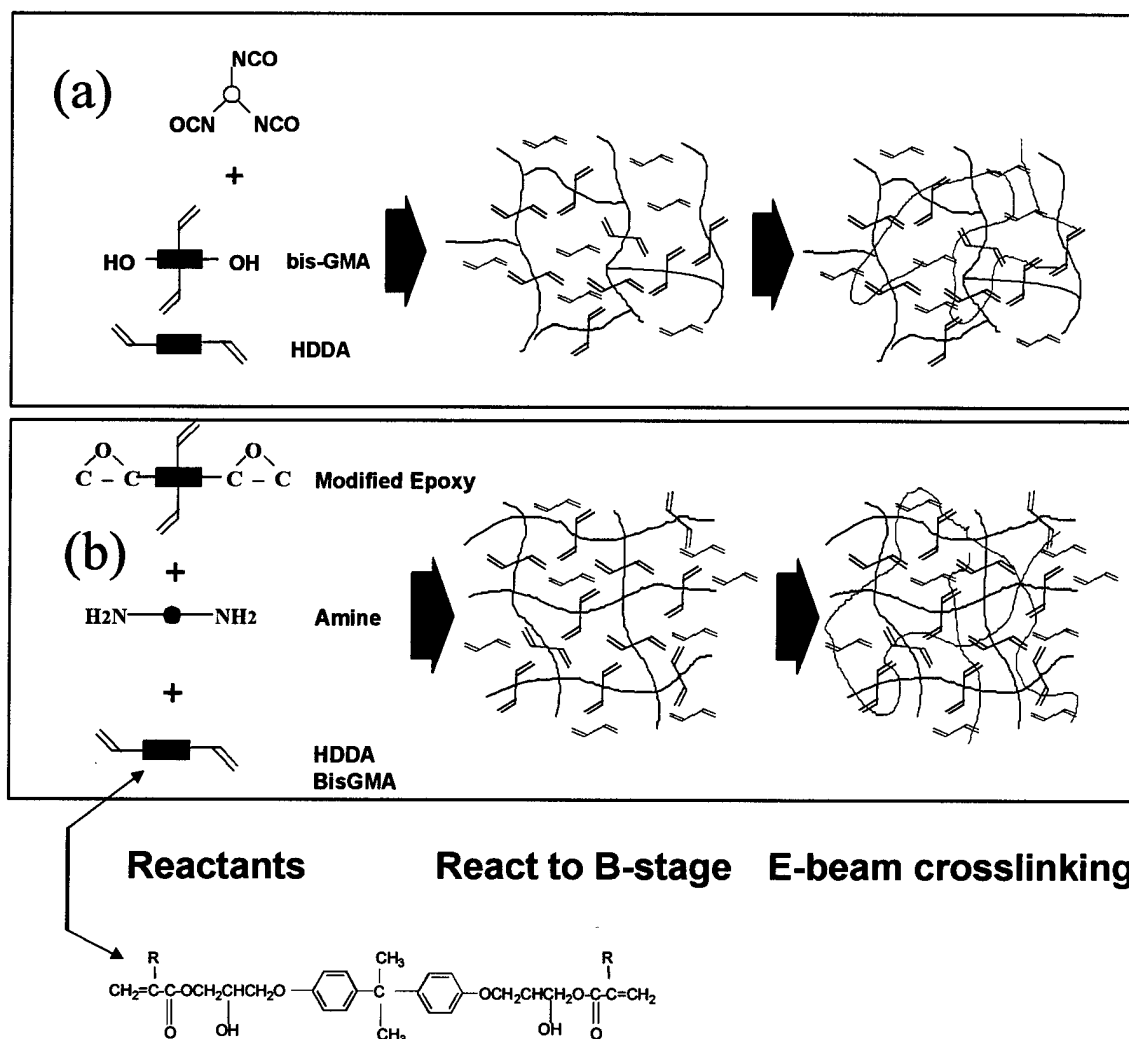
Figure 11: Two chemical approaches to B-staging of EB-curable resins.
(a) A urethane system with reaction of hydroxyl and isocyanate groups, (b) an epoxy system utilizing the epoxy-amine reaction. Resins of the urethane type have designations UA-# where # represents a specific formulation. The epoxy resins are designated EAL-#.

The B-stageable urethane system shown in Figure 11(a) gives good neat resin and composite properties including glass transition temperature Tg~200°C and shrinkage of less than 4%. This is shown in Figure 12. We have designated these system as UA-#. Samples of UA-36 resin have been sent out to several potential buyers.

However, a difficulty with using the acrylated urethane UA-# systems is the requirement to avoid moisture which can react with the isocyanate to form bubbles (voids) in the composite. This requires careful drying of the cloth or fiber before impregnation.
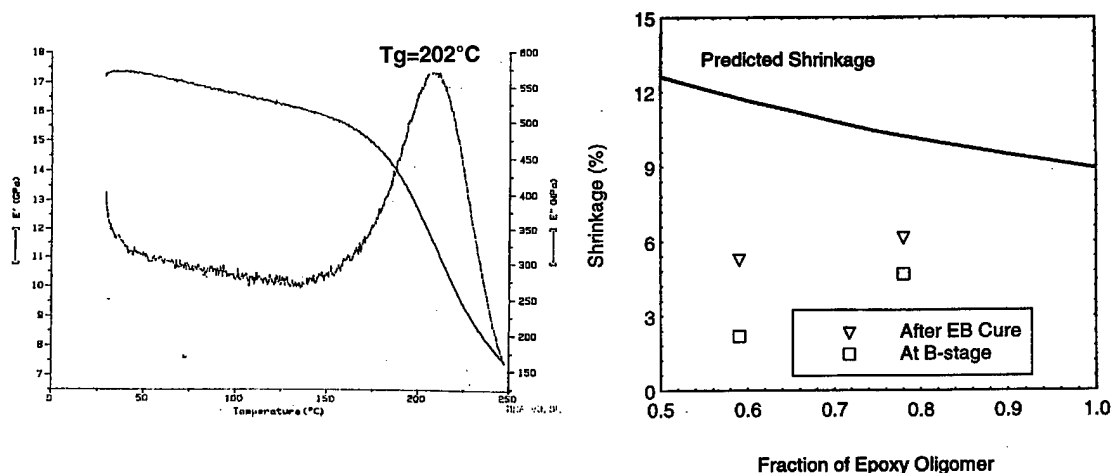
Figure 12: Thermal and shrinkage properties.
The B-stageable urethane resin of Figure 11(a) has good thermal properties and lower shrinkage than expected. The low shrinkage is due to the interpenetrating network shown at the right of Figure 11(a).

To avoid the problems with using isocyanates, we formulated B-stageable resins using acrylated epoxy amine chemistry as shown in Figure 11(b). We have designated these resins as EAL-#, where # is the formulation number. These systems have lower void content than the urethane resins, but also lower use temperatures. Neat resin and composite date for the urethane and two epoxy systems are shown in Table 2, with results after environmental aging shown in Table 3.

Property	Vinyl Ester (Baseline)		Urethane Acrylate (EB Cure)		Epoxy Acrylate (EB Cure)	
	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	---

Table 2: Neat resin and composite properties.

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All data are from B-stageable EB-curable resins with S2 glass reinforcement and 933 sizing.

Test Conditions	Vinyl Ester (Baseline)	Urethane Acrylate (EB Cure)	Epoxy Acrylate (EB Cure)
Moisture Uptake at equilibrium (50°C and 85% RH in wt %)	0.14	0.21	0.31
Tensile strength (% retained after environmental testing)	83	76	88
Compression strength (% retained)	92	75	104
Flexural strength (% retained)	82	71	87
In plane shear (Iosipescu) (% retained)	87	93	95
Interlaminar (SBS) strength (% retained)	89	88	94
T_g as prepared (°C)	110	139	113
T_g after postcure 1 hr at 150°C (°C)	-	189	135
T_g after boiling 24 hours in water	120	176	124
Weight gain (%)	0.24	0.35	0.50
T_g after postcure and water boil (°C)		201	134
Weight gain (%)		0.41	0.54
Fiber Vol Fraction As Prepared	~50%	~50%	~50%
Void Content As Prepared	0.5%	2.5%	0.6%

Table 3: Neat resin and composite properties after environmental aging.
All Results are for B-stageable EB-curable resins with S2 glass reinforcement with 933 sizing.

2.2 Dual Cure Adhesives

One type of EB-curable adhesive developed under this SBIR for joining automotive body parts is an elastomeric dual-cure formulation including an interpenetrating network (IPN). This system has a use temperature ranges as high as conventional high temperature adhesives used for bonding structural assemblies, bonds quickly by EB without heating and without causing warpage from thermal stresses. These elastomeric dual-cure adhesive formulations typically have lap shear strengths of above 1500 psi and tensile elongation to failure values of greater than about 50% within the use temperature range of the fully cured adhesive. The use temperature range for automotive bonding is quite wide, from approximately –40° to +100°C. The minimum temperature of the use temperature range is reached when the adhesive becomes too

brittle for its intended application, and the maximum temperature is reached when the adhesive loses its strength, i.e., the tensile elongation values fall below the approximately 750 psi required values for automotive bonding. By "interpenetrating network," we mean materials such as defined by Sperling in Ref [13]. That is, an IPN is any material containing two polymers, each in network form, in which grafts (or covalent bonds) between networks may occur to a greater or lesser extent. Generally, the deliberately introduced cross-linked sites outnumber the accidentally introduced graft sites. The formulations developed under this SBIR include a first network joined by urethane linkages and second network including urethane groups joined by a cross-linked polyacrylate network.

Our dual-cure adhesive formulations are electron-beam radiation curable and heat curable at relatively low temperatures. The elongation to failure values of the formulation are achieved with both soft and hard phase-separated domains in the fully cured adhesive, which ensure that the fully cured adhesive exhibits rubbery dynamic mechanical behavior within its use temperature range. The soft domains comprise mainly miscible groupings of polyol chains of a polyurethane and a urethane acrylate oligomer, and have a glass transition temperature well below the use temperature range of the fully cured adhesive. The hard domains comprise isocyanate diol or triol chains, and/or acrylate polymer chain segments, and have a glass transition and/or a melting temperature above the use temperature range of the fully cured adhesive. SRL has submitted a patent for these adhesives, and is offering the materials for sale through its Electron Solutions Inc. subsidiary. More information can be found on the web at the address of Ref. [6].

Section 3. Thick-Section Curing of Armor Panels

The Composite Armored Vehicle (CAV) Advanced Technology Demonstrator is an armored combat vehicle which is the first to use a fully integrated armor and structural composite hull [1]. A picture of the CAV and a side skirt armored panel that was prepared using EB curing is shown in Figure 13, and EB-cured panels after ballistic testing are shown in Figure 14 and Figure 15. The side skirt panels are composed of

layers including base composite, ceramic tile armor and signature protection. Each side skirt is approximately one square meter and was fabricated using low cost, wood tooling.

The EB-cured demonstrator panels performed as well in all respects as side skirts fabricated using conventional resins and heat curing at United Defense L.P., the prime contractor on the CAV-ATD. As seen in Figure 15, the rear side of the panels shows the stitched laminate, which helps prevent delamination of the composite upon ballistic impact. More details on the ballistic testing are given in the next section.

Deflection Limiting Bumper

Armor Panel

Flexible Skirt

Isometric from Track Side

Figure 1: Spare armored side skirts were fabricated using EB composite curing. The process showed the ability to room temperature cure multiple layers of dissimilar material in a thick composite without residual thermal stresses.

Armor panels consist of seven layers including base composite, rubber, adhesive, ceramic tile, EMI shielding and signature protection.

Center Panels are Interchangeable

501dg005

Figure 13: Composite Armored Vehicle panels were fabricated using electron beam curing and "Tool-Free" B-stageable EB-curable resins.

The CAV armor panels were fabricated by combining vacuum assisted resin transfer molding (VARTM) with electron beam curing, using methacrylated urethane and epoxy resins formulated by SRL and UD-CCM [14]. These novel resins are designated "Tool-Free" because composites impregnated with these resins can be removed from the mold prior to electron beam curing. This allows the use of low-cost low-temperature tooling or tooling which degrades upon electron beam exposure. Although wood was

used in forming the CAV panels, SRL and others have also used epoxy, plaster and foam [15].
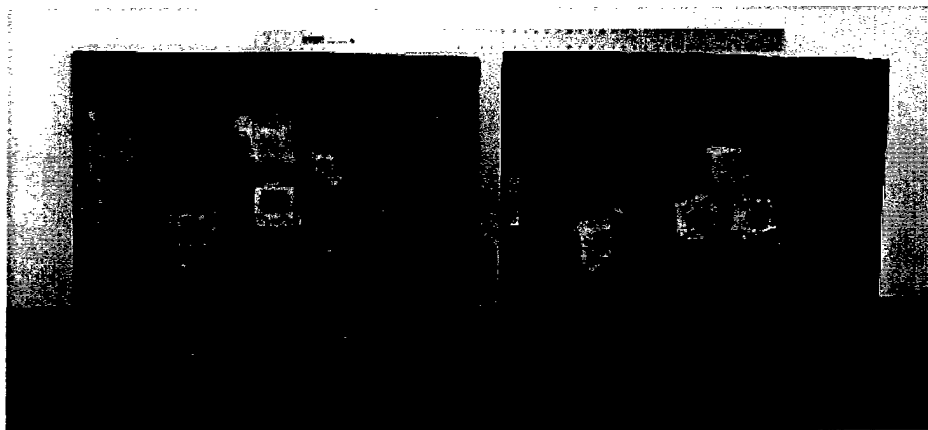

Figure 14: EB-cured CAV panels after ballistic testing at United Defense (front).

Figure 15: CAV panels after ballistic testing (rear).

The SRL "Tool-Free" resins are designed to cure in two steps, forming an interpenetrating thermoset network on complete cure. As shown in Figure 11, a low temperature thermal reaction to B-stage occurs forming either a urethane or an amine-epoxy network. The figure shows network formation at B-stage and after EB cure. The resin thermal and mechanical properties compare favorably with vinyl esters, exhibiting a glass transition temperature (T_g) of approximately 60°C at B-stage and T_gs higher than the vinyl esters after EB cure. The panel shown in Figure 3 contains resin formulated with low-cost epoxy acrylate formulated from a low-temperature epoxy. The T_g of such a system is 130-140°C. Use of a higher cost epoxy result in a T_g of greater than 160°C. The dynamic mechanical spectra for such a system is shown in Figure 4.
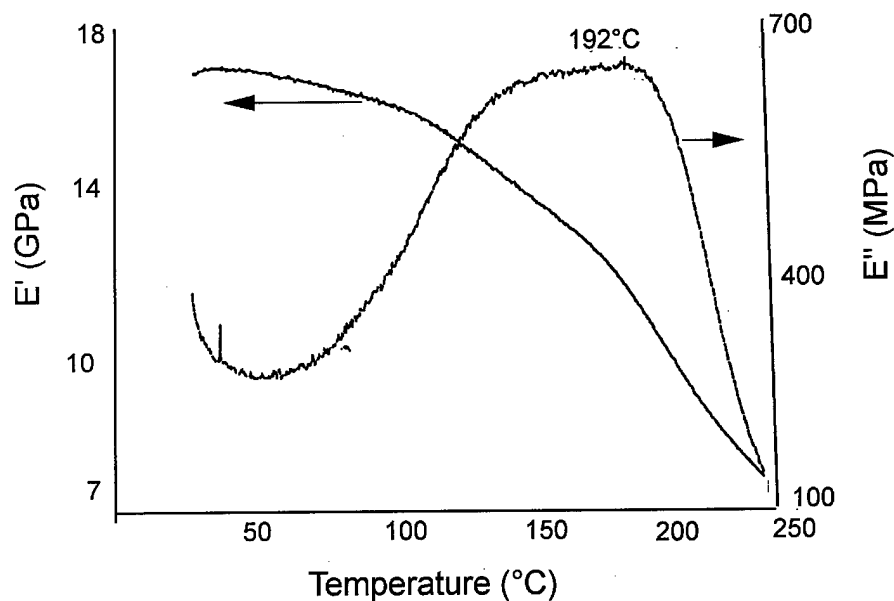
Figure 16: Dynamic mechanical analysis (DMA) for the B-stageable acrylated urethane resin system shown in Figure 11.
The listed glass transition temperature of 192°C is based on the peak of the loss modulus. Other methods to obtain T_g from the DMA data give values greater than 160°C.

For a composite property comparison we chose as a baseline the Dow Derakane series of vinyl esters. Composite composed of these resin reinforced with woven or chopped glass roving are commonly used in low-cost vehicle applications as well as industrial equipment and structures such as absorption towers, process vessels, storage tanks, piping and exhaust hoods. Mechanical properties of the EB-cured composites (both strengths and moduli) exceed those of the vinyl ester baseline. EB-curable composites were prepared using Owens Corning S-2 glass roving with a 933 sizing. Of the commercially-available sizings, the 933 is the one most compatible with the SRL "Tool-Free" urethane acrylate resin [16].

EB-curable composites were fabricated from "Tool-Free" resins based on both acrylated urethane and acrylated epoxy chemistry. Composites impregnated with both resin systems demonstrated superior compression modulus, flexural modulus, Iosipescu shear and short beam shear compared to the vinyl ester thermally cured baseline. Of the two systems, composites containing the urethane acrylate show approximately a 20%

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higher compression modulus and flexural modulus compared to the epoxy acrylate. The other mechanical properties are approximately the same for the two EB-curable chemistries, exceeding the baseline composite by 20-30%.

Environmental testing was performed on the three types of composites and the results are shown in Table 2. Mechanical and thermal properties in the table are compared to their values before environmental aging. Test specimens were aged at 50°C and 85 percent relative humidity until the weight gain reached an equilibrium value. While the urethane acrylate and the epoxy acrylate gained more weight than the vinyl ester, all three materials gained less than one percent. The vinyl ester and urethane acrylate based composites retained approximately 80% of their tensile strengths after the environmental aging, while the epoxy acrylate composite retained nearly 90% of its initial tensile strength. In compression, both the vinyl ester and the epoxy acrylate retained more than 90% of their original moduli, with the urethane acrylate decreasing to 75% of the original value. In flexure, the urethane acrylate composite decreased to 71% of its original value. This behavior is due to the difficulty in achieving complete reaction of the moisture sensitive isocyanate (NCO) groups during the B-stage and subsequent reaction of the NCO functionality with moisture during the environmental aging.

3.1 Ballistic Testing of CAV Panels

Ballistic testing was performed to evaluate the SRL E-Beam processed skirt backing and compare it with laminates made with the prepreg process. Two SRL armor samples were submitted to UDLP Terminal Ballistic Laboratory for testing with an artillery simulant. The results of this testing were:

1) The alumina ceramic materials used in the SRL targets did not match the penetration resistance and multi-hit capability of previously tested prepreg targets that used high cost SiC ceramics.

2) The SRL laminate alone matches the performance of the current prepreg in supporting ceramic tile to resist penetration and provide multi-hit performance.

3) Although delamination is difficult to measure and compare, the SRL panels appeared to delaminate slightly more than the current prepreg or a VARTM, but the delamination was small enough so that it did not degrade multi-hit capability.

4) The alumina ceramic showed-slightly better performance than Lanxides metal matrix ceramic although alumina is a heavier material. Neither ceramic matched the performance of the hot pressed silicon carbide normally used.

5) The stitched backing appeared to limit delamination, but it was not determined whether stitching enhances penetration resistance.

The configuration used was the standard set-up used to evaluate Composite Armored Vehicle (CAV) skirt armor. The SRL panels were spaced 17" from a panel consisting of 5/8" PPS bonded to a 1/2" 977-2 Epoxy used to represent the vehicle sponson. A single piece of 0.020" aluminum witness sheet was placed 6" behind the set-up. Any particle passing completely through this witness is a "complete penetration."
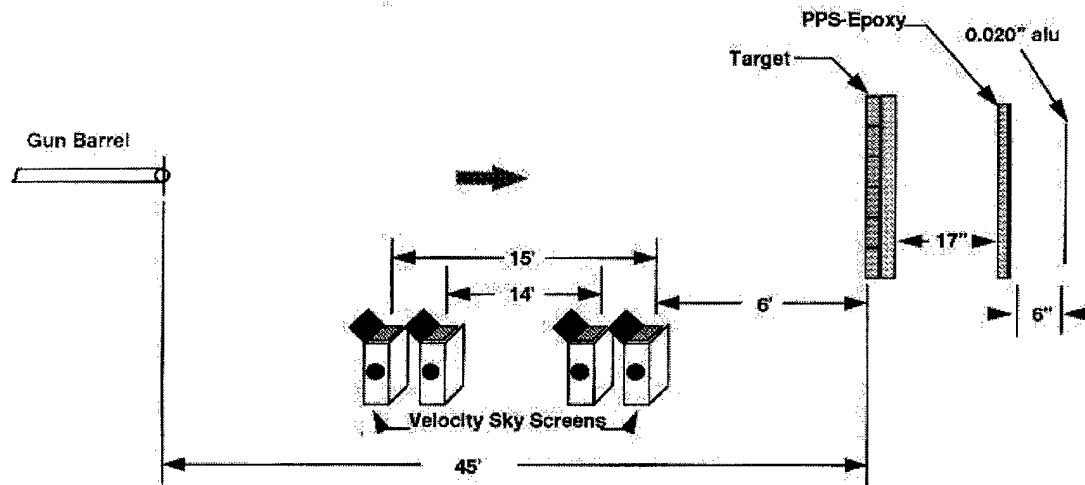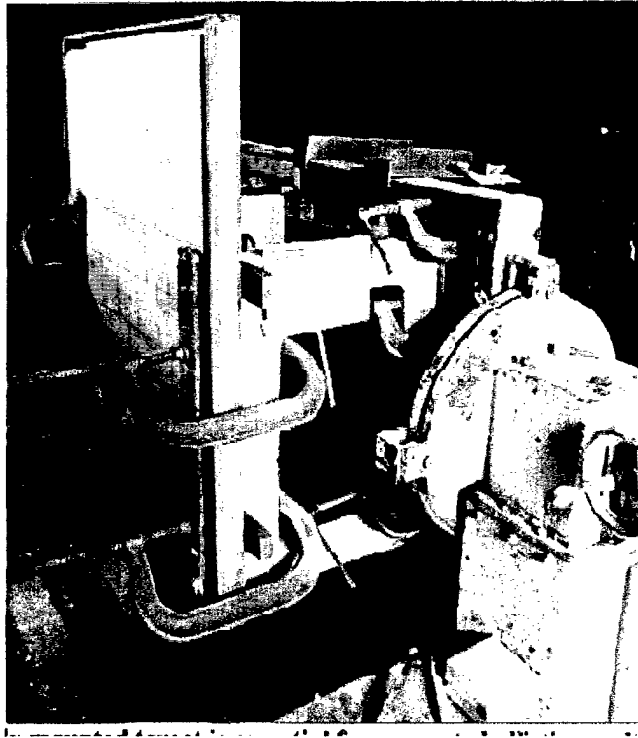

Figure 17: Ballistic test set-up.

Figure 18: Target mounting for ballistic testing.
Rubber lined steel bars were used to reduce point loading of the ceramic.

The tests were performed at UDLP's Terminal Ballistic Laboratory using a Mann barrel to fire Fragment Simulated Projectiles (FSP). The ballistic test setup is shown in Figure 17. The target shown in Figure 18 was mechanically clamped to a test rack at a zero degree obliquity. The target was placed in a frame fabricated from 3/8" angle iron to support its edges. The weapon was also verified to be zero degrees. The velocities were measured using two sets of Weible Sky Screens. Drag coefficients and atmospheric conditions were used to derive impact velocities for the reported velocities.

Two tests were performed to determine the performance of the EB curing process. Performance was measured by partial and complete penetrations on a similar shot pattern at the CAV shot velocity. A summary of the test results provided in Table 4 below.

Table 4: Ballistic Results

Target	Ceramic	Backing	Velocity Difference (1)	Firing Record	Results pp/cp (2)
SRL-1	Alumina	S-2 24oz	+66	97035	3/1

SRL-2	Metal	S-2 24oz	+67	97034	1/3
	Matrix SiC	stitched			

(1) average velocity difference from CAV requirement in ft/sec

(2) PP = partial penetration, stopped in PPS-Epoxy, CP = complete penetration

For SRL-1, Shot#1 impacted a center tile and stopped in the PPS-Epoxy panel. The PPS-Epoxy panel had a delaminated area of 8" x 13" and a 1/4" back bulge. Shot #2 impacted a tile edge and stopped in the PPS Epoxy panel. The PPS-Epoxy panel was delaminated out to the edges and had a back bulge of 3/8". The third shot impacted a tile edge and was a complete penetration. To verify edge performance a fourth shot was placed outside the shot pattern triangle on an edge. This resulted in a partial penetration. This target demonstrated penetration resistance at centers and edges. The third shot complete penetration is attributed to tile cracking due to adjacent tile impacts, not to backing performance.

For SRL-2, a similar hit pattern was used on this Lanxide metal matrix silicon carbide hex tile target. Shot #1 a center tile impact resulted in a partial penetration. The round stopped in the PPS-Epoxy panel. The delaminated area measured 8" x 9" with a 1/4" back bulge. Shots 2&3 were complete penetrations. A fourth shot on a tile edge was requested to verify edge performance. This shot was also a complete penetration. This targets poor edge performance is attributed to the ceramics, not the backing.

These results are very similar to CAV target SSA1-6 from April 12, 1995. This target successfully defeated five out of six rounds with an average velocity of +164ft/s above the requirement. This target was also fired using the similar shot pattern.

Section 4. Bonding of Automotive Panels

4.1 Requirements

The baseline materials for bonding together automotive body panels are heat-curable adhesives. Conventional heat-curing adhesives require many minutes to bond. Total bonding time includes the time to heat the material at the bond-line plus the time to

cure the adhesive. Plastic auto bodies such as the CCV are effective insulators, preventing heat from reaching the bond-line. Oven or forced hot-air temperatures must be limited to avoid deforming or melting the thermoplastic. These effects combine to give hot-air bonding times of many minutes, whereas auto manufacturers prefer cycle times under two-minutes.

Some of the bonds in the CCV join the plastic to a steel frame chassis. After joining with heat-curable adhesives, some sections of these bonds and near-by composite can crack when cooled to room temperature. The cracking is due to the thermal expansion mismatch, caused by the much larger contraction of the plastic than the steel during cooling.

To avoid these problems with heat-curable adhesives, some manufacturers have formulated adhesives that cure at room temperature. Once mixed, these systems have very short working life before they harden. Such systems are well suited to bonding of small areas, but are very difficult to use on large areas such as auto bodies.

What is preferable for this application is a true room temperature "command cure," which provides extremely rapid curing, but only once the adhesive, parts and tooling are aligned in place. Curing of adhesive with electron beams provides this processing flexibility.

Although the material, process and cost requirements for adhesive bonding of the CCV plastic body panels are still evolving, target values have been established for key properties. Key material properties are: initial lap shear strength immediately after curing, final lap shear strength as a function of temperature, shear strength as a function of bond-line thickness, adhesive elongation to failure at room temperature and elongation at elevated temperature. Processing requirements include adhesive working time and curing time. The price of conventional automotive adhesives establishes a cost target.

Conventional cars are tack welded at many locations along the frame. Although these welds have very high strengths, they only cover a small total area. Using typical tack weld strengths and dividing by the CCV bonding area gives a lap shear strength requirement between 500-750 psi. An upper limit to the required lap shear strength is the value at which the surface of the bonded composite suffers an interlaminar failure. This value is between 1500-2000 psi.

In many adhesive applications, full bonding strength is not immediately needed. For example, urethane windshield adhesive/sealant takes several days to fully cure. Such is also the case with the bonding of the CCV. It is sufficient for the CCV that the strength immediately after bonding be at least half of its final value.

Automotive adhesives for structural bonding are much more flexible (although not nearly as strong) as those used to bond aerospace structures. It is difficult to maintain tight dimensional tolerances in molded parts, so the bond-line thickness vary considerably in the CCV (and in automotive applications generally.) The adhesive for the CCV thus has the additional roles of shock absorber and of caulk or sealant.

Figure 19 shows the results of a simple slab model to determine elongation requirements for adhesive bonding of the CCV PET to the steel chassis. The adhesive requires sufficient elongation to be able to accommodate the maximum expected end-use thermal expansion mismatch between the PET and the steel. For the designed CCV bond-line thickness, the figure shows that an adhesive elongation to failure of approximately 100% is required.
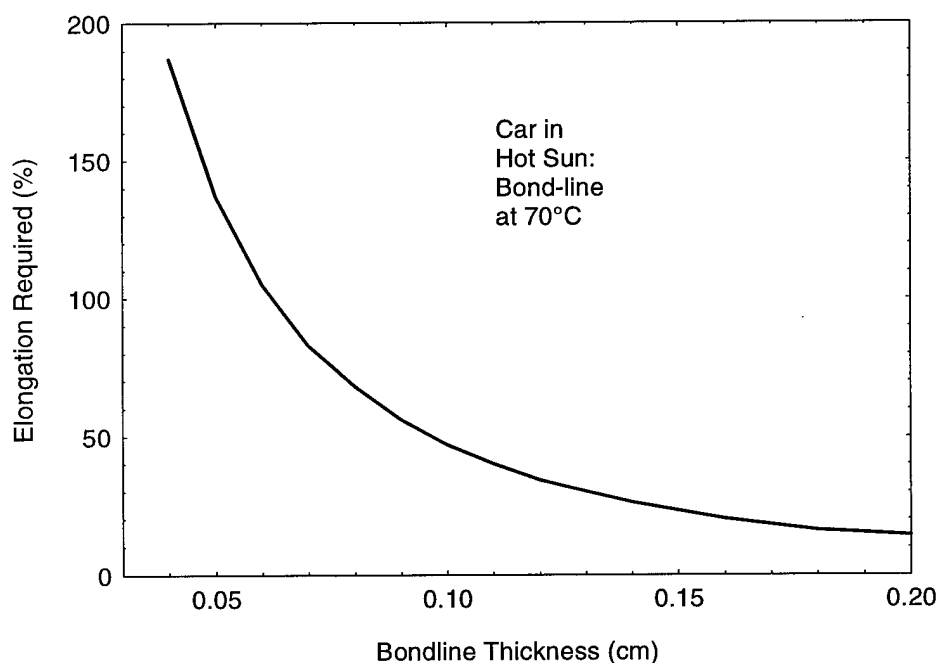

Figure 19: Thermal expansion mismatch in the CCV.
The CCV utilizes high thermal expansion PET bonded to a steel chassis. When the car is heated, thermal expansion mismatch must be accommodated by elongation of the adhesive.

To meet process and cost requirements, the EB-curable adhesive for bonding the CCV must meet four additional criteria: 1) It should have high room temperature viscosity (>25,000 cP) to prevent sag on vertical surfaces. 2) If formulated from a two-component reactive system to slowly react at room temperature, it should have a long pot life (>45 minutes). 3) When irradiated by electron beams, it should achieve half its final strength in less then two minutes. 4) The adhesive system cost should be comparable to existing heat-curing urethane and room temperature curing acrylic adhesives currently used for automotive applications.

4.2   Bonding Results

The first step in demonstrating the usefulness of EB bonding for the CCV application was to demonstrate that EB processing does not degrade the thermoplastic.
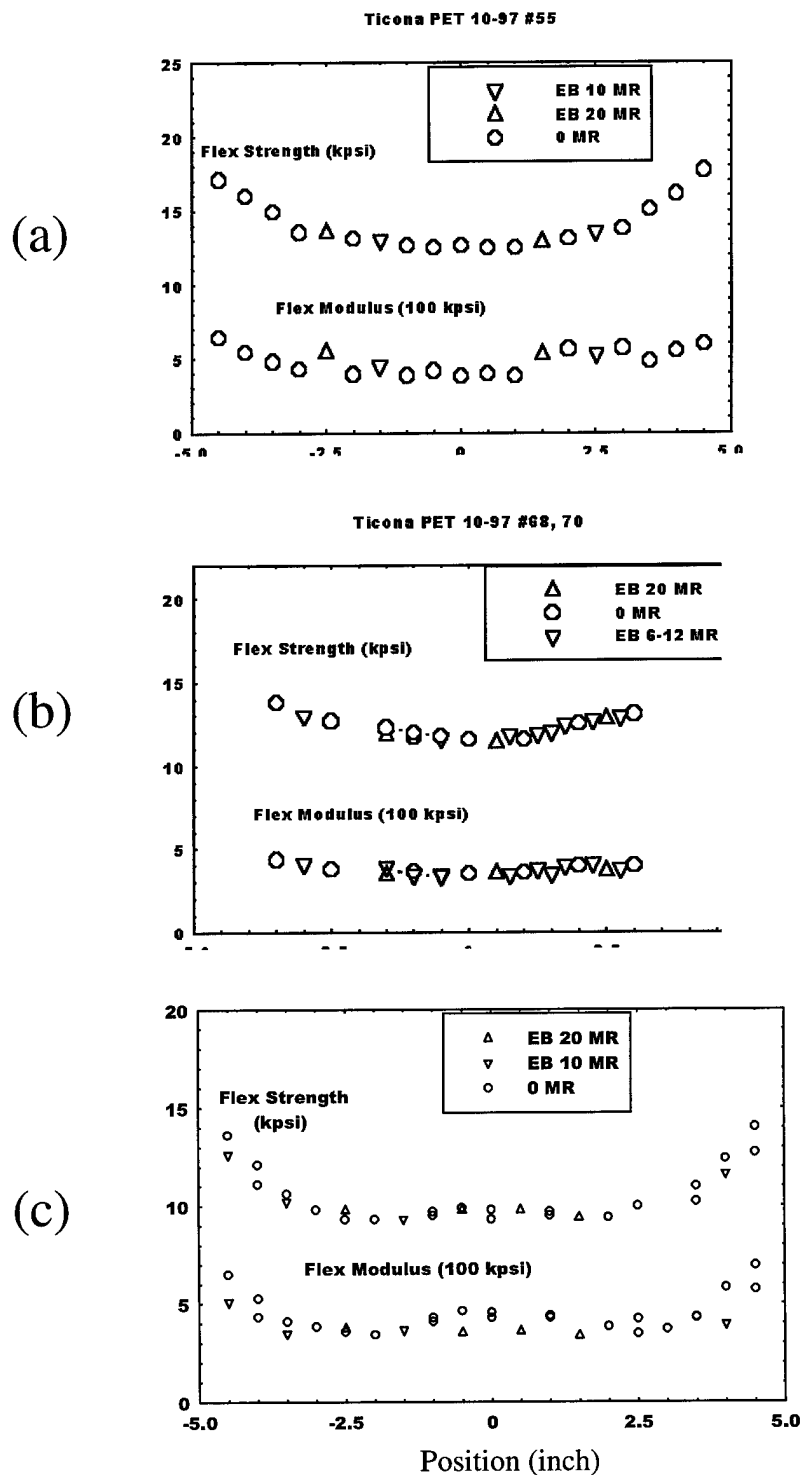
Figure 20: EB irradiation of the thermoplastics used for the Chrysler CCV.
No degradation in the flexural strength or modulus was seen. The variations across the panel are due to alignment of the glass reinforcement fibers during molding. Eliminating these inhomogeneities is one of the current goals of the Chrysler CCV development program.

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Novel electron beam curable adhesives were formulated to meet the requirements described in Section 4.1. The results of mechanical and thermal testing are described in this Section. Novel electron beam equipment was also developed which irradiates specified curved paths. Such equipment efficiently cures the adhesive along the bond-line without irradiating the remainder of the automotive body.

The type of adhesive developed for this application is a phase-separated dual EB/room temperature cure elastomeric formulation. The adhesive is a two-component system containing both EB-curable acrylated oligomers and monomers as well as urethane prepolymers, which react with an isocyanate at room temperature to form a urethane network. They are similar in concept and chemistry to the B-stageable "Tool-Free" resins used for the CAV: Those systems reacted to a solid at room temperature and then achieved full properties by EB-cure, whereas the SRL dual-cure EB-BOND™ adhesives are first cross-linked by EB and then complete a room temperature cure. More details about this adhesive were described in Section 2.2.

There are two advantages to using a dual-cure adhesive for this application. 1) A dual-cure urethane/acrylic system can achieve the desired properties at lower cost than a purely EB-curable system. 2) If some fraction of the dual-cure adhesive receives less than the optimal radiation dose, it will still provide a sufficiently strong and elastic bond via the room-temperature urethane reaction.

Mechanical and thermal properties for one dual-curing adhesive system are shown in Figure 21 and Figure 22. The tensile strength and elongation of a blend of EB-curable urethane acrylate and room temperature curable urethane was found to be relatively insensitive to the blend ratio, providing process flexibility. Lap shear strength does depend on the blend ratio, with an optimum for process and strength found to be near 50 percent by weight.

Figure 23 shows test panels made of the same thermoplastic material as the Chrysler CCV being prepared for EB bonding. Approximately two dozen of these panels were sent to SRL for testing. Bonding of actual CCV side panels was accomplished at SRL after the end of this program, as the next step in this demonstration. This is shown in Figure 24.
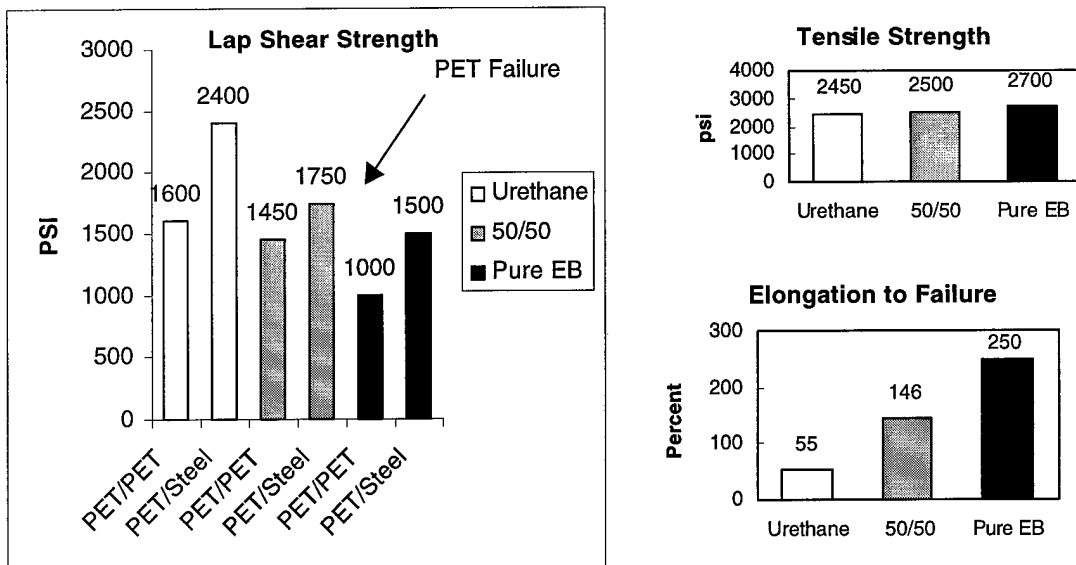
Figure 21: Mechanical properties of dual EB / room temperature curing adhesives. These adhesives were designed for automotive bonding of PET composites to themselves and to steel chassis. A 50% by weight blend of the EB-curing acrylate and the room-temperature curing urethane meets or exceeds all target properties. (Values listed were measured at room temperature.)
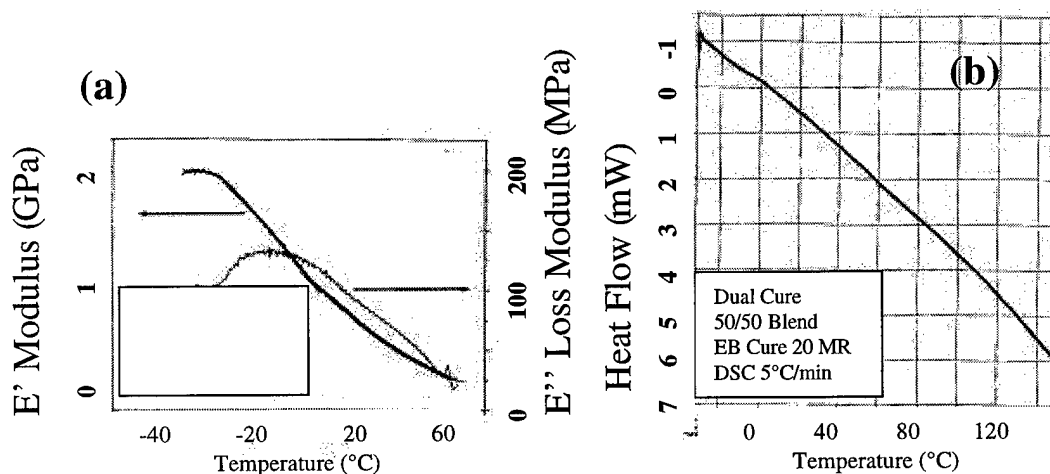

Figure 22: Adhesive thermal properties after 24 hours at room temperature.
(a) The DMA trace for the dual EB/room temperature cure adhesive is similar to heat-curable urethanes used for automotive bonding. (b) A lack of inflection points in the DSC trace shows full curing after EB irradiation and 24 hour age.
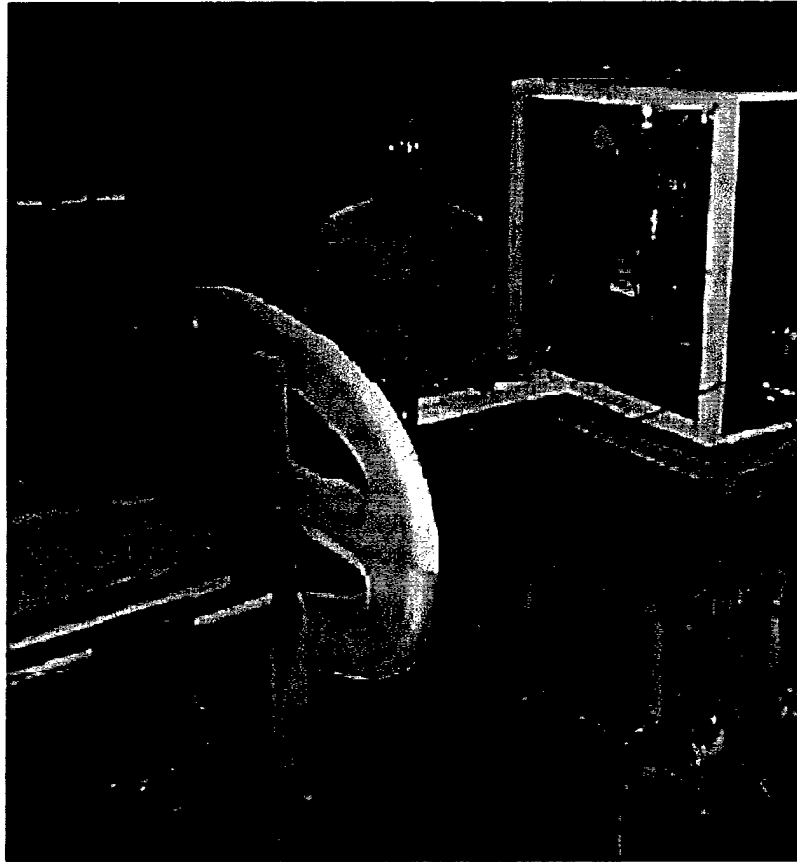
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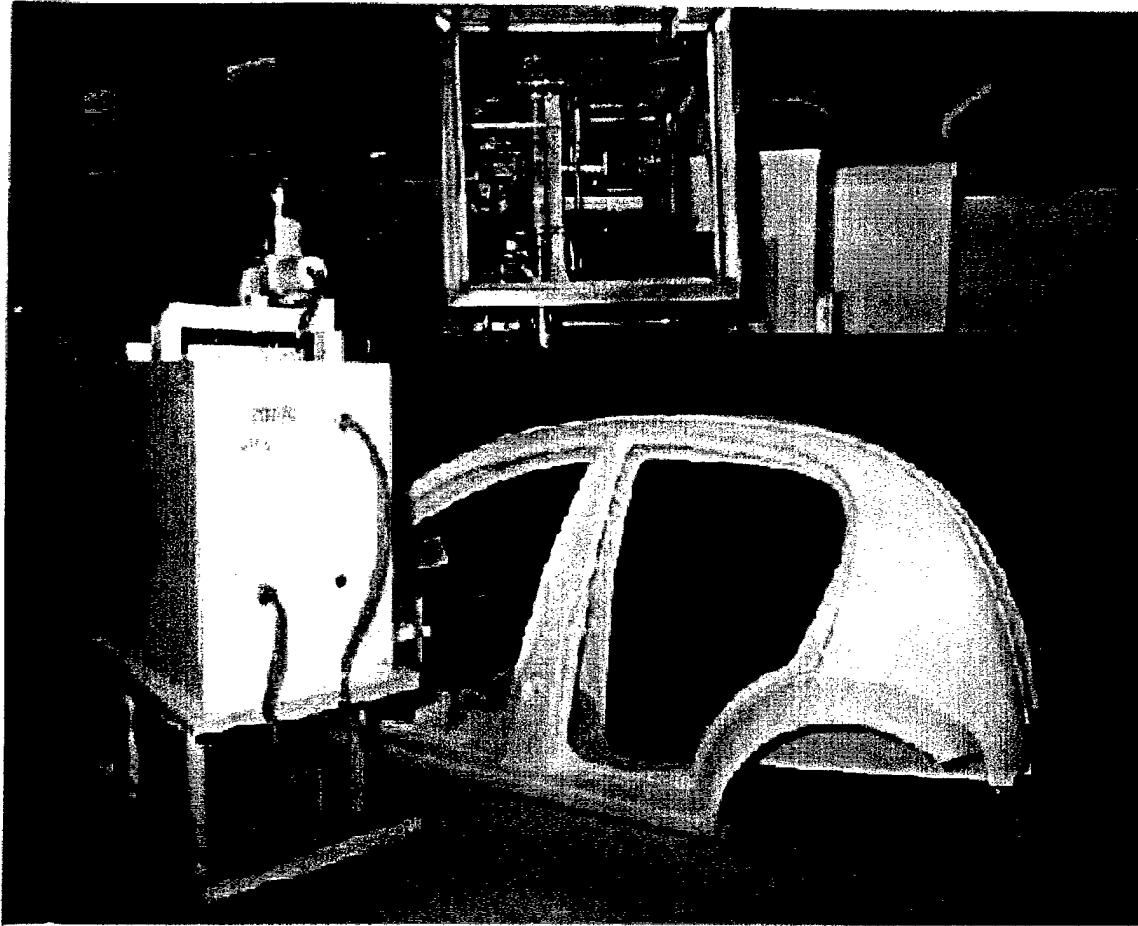Figure 23: Bonding of test panels made of the Chrysler CCV thermoplastic.

Figure 24: Bonding of Chrysler CCV side panels.
Bonding was done with EB-curable adhesive and EB curing equipment developed at SRL.

Section 5. Conclusions and Future Work

Electron Beam (EB) curing of resin and adhesive offers significant advantages for fabricating and bonding of fiber-reinforced polymer composites for ground vehicle structural components. The EB curing process reduces the time to cross-link the polymer matrix or the adhesive compared to conventional heat curing. The process allows curing at room temperature for high throughput and reduced residual stresses for good part fit-up. EB adhesive curing also prevents de-bonding of dissimilar materials that can occur during the cool-down cycle. As part of this SBIR program, Science Research Laboratory (SRL) has developed resins, adhesives and electron gun technology for high-energy electron beam curing and bonding of composites.

During this program, two demonstrations showed ground vehicles that benefit from the use of electron beam cured composites and adhesives. Side armor skirts for the Army's Composite Armored Vehicle (CAV) are complex parts composed of multiple materials. Spare armor panels were fabricated using electron beams to demonstrate thick section curing. The Chrysler Composite Concept Vehicle (CCV) is fabricated from thermoplastic resin injection molded body panels that are joined using adhesive bonding. Test portions of the CCV including the inner- and outer-side panels were bonded using EB-curable adhesive to demonstrate the advantages of high-speed low-temperature bonding for automotive fabrication.

The use of EB-curable composites and adhesives for ground vehicles is continuing into a commercial Phase III activity. SRL recently received approval of our US Patent application to protect the "Tool-Free" B-stageable EB curing process and materials. Chrysler (now Daimler-Chrysler) is undergoing re-organization as a German company, and has not yet decided the direction of its future R&D effort. SRL plans to continue to work with Daimler-Chrysler and with the other automotive manufacturers, who agree that EB bonding of plastic cars makes sense from both technical and cost points of view.

The adhesives developed under this program are also finding application in the aerospace community. Members of the Composite Affordability Initiative (CAI), a cooperative effort by the Air Force, Lockheed Martin, Northrop and Boeing, recently determined that SRL adhesives have the best properties of the currently available EB-curable materials. SRL personnel are also using dual-curing adhesive approaches developed under this SBIR to formulate a film adhesive for CAI.

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