ELECTRON CURING OF COMPOSITE STRUCTURES FOR SPACE APPLICATIONS

EXECUTIVE SUMMARY

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by

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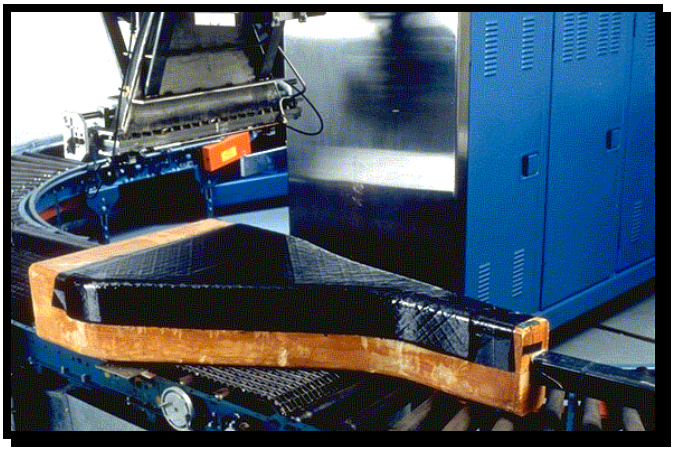
Introduction

This report summarizes work done for the U. S. Air Force Phillips Laboratory by AECL Technologies under contract F29601-95-C-0180. The objective of this program was to assess the potential of electron curing technology for the manufacturing of space structures. The potential of electron curing to lower composite costs and improve product performance have been known for several years. In this program, we examined whether electron curing has a role for manufacturing affordable, high-quality, space structures.

Electron or EB curing uses high-energy electrons from an industrial accelerator to initiate polymerization and crosslinking reactions in suitable polymers. Many benefits have been identified for fiber-reinforced composites when electrons are used rather than thermal energy for curing. These include reduced residual stresses that result from curing at ambient or subambient temperatures, shorter curing times for individual components, improved material handling, and possible process automation, all of which translate into improved product quality and/or lower production costs.



EB Curing of Bulkhead

EB curing has the potential to process complex structures faster, with more control, and with less risk than autoclave processing, while providing more design and tooling freedom. Technologies such as fiber placement and vacuum assisted resin transfer molding (VARTM) can be combined with EB curing to produce affordable space structures with superior properties. Several technical issues have to be addressed to fully evaluate the potential of EB curing for space structures.

These issues include:

- the effect of varying the electron curing temperature on the performance of composites over the full temperature range expected in space.
- the mechanical property requirements that must be met in EB-cured products.
- the effects of atomic oxygen, radiation, and high vacuum on the performance of electron-cured composites.

The Issues

Space applications for composites have developed rapidly over the past 10 to 15 years, being led by NASA and the DOD. Composites are now the leading candidate materials not just to save weight, but to increase system performance. Their high specific strength and stiffness, combined with low coefficient of thermal expansion (CTE), cryogenic stability, load tailorability, and high specific damping capacity, make them particularly attractive for high-precision space structures.

INTELSAT 8 Satellite

The design lifetime of most early spacecraft was relatively short (5-7 years), making material changes in space small. However, the current trend toward longer lifetimes (ultimately to 20-25 years) has resulted in a substantial interest in long-term durability of composites in the space environment.

The two major use orbits for structural materials are low-earth orbit (LEO), located in the 400-800 km range, and geosynchronous orbit (GEO), located at about 36,000 km. For LEO applications, the major exposure parameters involve atomic oxygen (AO), solar ultraviolet (UV) radiation, micro-meteoroids and man-made debris, and continuous thermal cycling. For GEO, where long-service-life products are usually needed, ionizing radiation, consisting of high-energy electrons and protons, thermal cycling and solar UV, place stringent durability demands upon materials. The synergestic effect of all of these environmental conditions can also be significant. A fundamental understanding of space environmental effect on composites is essential for confident design of long-life space structures.

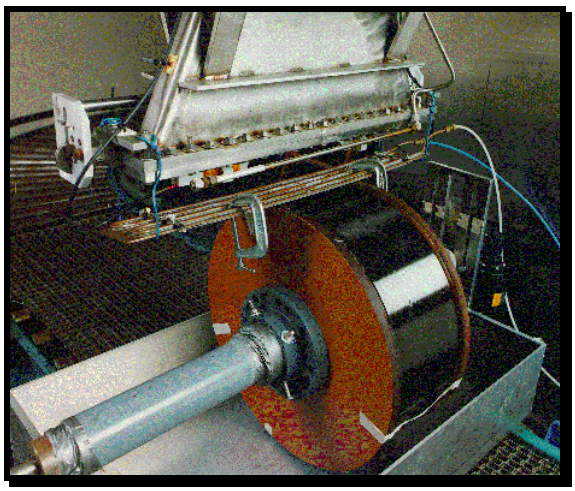
EB Curing Process

Accelerators produce a beam of electrons that are directed on to a product. The high-velocity electrons lose their energy by interaction with the target materials. There are several general types of accelerators, with beam powers ranging from 50 to 200 kW. A typical EB-curable carbon-fiber-reinforced epoxy laminate can be cured with a dose of about 100 kGy (10^5 J/kg) (Saunders et al., 1993a). A commercially available 50-kW accelerator can provide this dose to about 900 kg/h of material. In comparison, a typical autoclave can cure about 200 kg/h of material. Thus, the production speed for a 50 kW accelerator to irradiate composites far exceeds that of

thermal curing with a typical autoclave, even though the products are cured one at a time during EB curing, compared to large batches in autoclaves.

Unique Features

The beam penetration limit must be considered when determining the applicability of EB curing for composites. EB penetration is a function of beam energy and product density. The electrons, or X-rays generated by the electron beam, must also penetrate any vacuum bag and/or pressure vessel if these are required for manufacturing the component. The maximum composite thickness (density = 1600 kg/m^3) that can be treated uniformly is estimated to be 21 mm for a 10-MeV EB and 160 mm for the X-rays (3-MeV) generated from the beam (Saunders, 1994).



X-Ray Curing of Thick Product

Metal inserts may also be included as part of the lay-up, depending on their position in the product and their size. Both prepreg and wet lay-up can be used for EB-cured laminates. EB curing is very well suited for all products that can be laid-up in the specified shape and then debulked at an elevated pressure.

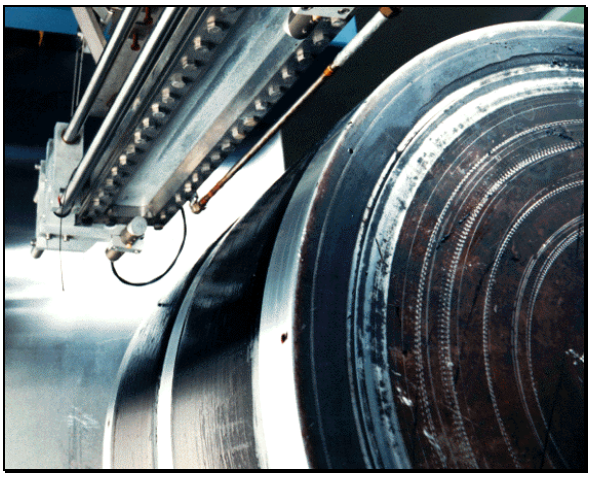
Very little resin flow should be expected in a composite during EB curing. Debulking/ consolidation under pressure, combined with vacuum-bagging, produces a stable, low-void composite product. EB curing under pressure, although possible, is considered impractical for most products, because two of the benefits of EB curing, the overall production speed and the simplicity of the process, are lost. A notable exception is selected products that have been manufactured using an internal bladder to provide pressure. Once the product has been consolidated, it is vacuum-bagged, using standard materials and procedures, and transported to the accelerator facility for curing. The beam is directed over the surface of the product in a prescribed pattern to ensure that the surface is uniformly treated. The dose per pass is set such that the product does not exceed the specified temperature (usually 50°C).

Two of the factors that contribute to more efficient material handling of EB-curable materials are: (i) the ability to handle the resins at room temperature makes it easier to prepare prepregs, and to fabricate products from them; and (ii) the ability to EB cure each item as it gets fabricated, reduces the space requirements for storage of the uncured items. EB curing also allows products with different resins requiring different doses to be processed one after the other. In thermal curing, all the contents of the autoclave need to have the same curing cycle.

Products that contain temperature-sensitive materials, e.g., foam or honeycomb with low melting point polymers, or mixtures of fibers (such as mixed laminates with carbon fiber- or aramid fiber-reinforcement) can be easily EB cured without dimensional distortions. Such laminates (up to 15 cm thick) have been produced by EB curing (Saunders et al., 1994).

Processing Issues

Traditional fabrication methods, including filament/tape winding, pultrusion, resin transfer molding, and lay-up and/or tape placement, can be combined with EB curing. Filament/tape winding is particularly well-suited to be combined with EB curing. High winding rates can make use of the available energy, and products can be cured while they are being remotely wound, either to increase the overall production rate to lower costs, or to improve the quality of a part by eliminating distortions from sagging or fiber movement. Unique mandrel materials, including cardboard, wax and polyethylene, can be used because thermal stability is not required. Standard filament winding equipment is used. For wet winding, the resins are impregnated at ambient temperature to standard loadings of 40 to 45%. The extended pot life of the resins allows the entire bath to be prepared prior to winding.



EB Curing a Wound Product

Combining EB treatment with pultrusion has the potential to increase the pulling speed. Pulling speed no longer depends on thermal conduction into the laminate, but depends on the accelerator power. Products can be laid-up using standard procedures developed for thermally cured composites. All standard core material, including honeycomb and foam, are suitable for EB curing. Debulking/consolidation under pressure, combined with vacuum-bagging, produces a stable, low-void composite product.

Over 600 different materials or various material formulations materials have been examined as potential tooling materials (Norris, 1996). Composite tools are, by far, the most radiation-resistant materials, with the polyimide systems exceeding a dose limit of 200,000 kGy or 2000 cure cycles. The epoxy composites have a limit over 100,000 kGy. The dose limits for composites are significantly higher than the limits for the matrix polymer, suggesting that damage to the polymer-fiber interface play an important role.

Resins

EB-curable epoxies constitute a unique class of polymers that can be rapidly cured to produce material properties that meet or exceed the properties of high-performance thermosetting epoxies. Hundreds of EB-curable resin systems, including toughened formulations, are now commercially available. Formulating EB-curable epoxies involves mixing a cationic initiator at a concentration of 1 to 3% with conventional epoxy resins. Cationic initiators react when subjected to irradiation from ultraviolet light, ionizing radiation (x-rays or gamma rays), or a beam of high-energy electrons. Most resins exhibit physical and mechanical properties that meet or exceed the properties of the analogous thermosetting epoxies. It appears that the outstanding properties of these resins are caused by direct crosslinking of epoxy groups, resulting in similar or better properties than with thermoset resins. Table 1 summarizes the characteristics of the EB-cured resins currently available.

Table 1: Key Features of EB-Curable Epoxy Resins

Features	EB Beam-Curable Epoxy Resins	Thermosetting Epoxy Resins
Mechanical Properties	high-performance	high-performance
Manufacturing Costs (overall)	moderate (25-65% less than thermal)	high
Prepreg Storage and Handling	extended lifetime at 20°C	limited lifetime below 0°C
Environmental and Health Concerns	low	moderate to high (hardeners)
Material Shrinkage on Curing (%)	2-3	4-6
Volatile Emissions (%)	< 0.1	< 1.0
Glass Transition Temperature (C)	up to 400	up to 300
Residual Stresses	Very low	Moderate to High (thermal mismatch)
Water Absorption (%)	< 2	< 6
Production Throughput	Fast	Slow
Maximum Composite Part Thickness Limit In A Single Cycle	50mm (EB) 200mm (X-ray) 1mm (ultraviolet)	20mm (thicker parts can be destroyed by exothermic reactions)
Tooling Materials	metals, wood, ceramics, plastics, waxes, foams	metals, ceramics, graphite
Tooling Costs	low-moderate	moderate-high
Cure Time (10-mm-thick part)	Seconds-Minutes	Hours
Energy Requirements	low to moderate	moderate to high
Capital Cost (facility)	high	high to very high (autoclave)
Source Material Availability	Resins and Initiators Available	Resins and Hardeners Available
Material Cost - complete resin system ($/lb)	2-5 (commercial), 8-20 (high-performance)	2-4 (commercial), 8-20 (high-performance)

Fibers and Sizings

Carbon is the fiber of choice for most aerospace applications because of its superior balance of properties. Carbon fibers have been shown to be particularly suited to EB processing, since they exhibit excellent radiation stability, tolerating about 1000 times the typical curing dose. Aramid fibers are also unaffected by EB treatment to the typical curing doses, a consequence of its highly aromatic structure. The effect of EB treatment on the mechanical properties, density and chemical durability of glass fibers was shown to be negligible up to a dose of 3 MGy. The only visible effect was a discoloration. The use of organic fibers such as polyethylene or nylon fibers for reinforcing EB-cured composites must be done with caution, because the properties of the fibers are affected by the EB treatment.

There are unresolved issues concerning fiber finishes suitable for EB curing. Currently, G'sizing is the most compatible to current EB resins being developed. However, as performance requirements have increased, in both temperature and mechanical properties, there is a requirement for a more compatible EB resin finish.

EB Curing for Space Applications

A key objective of this program is to determine if the expected benefits of EB curing can be realized for manufacturing space structures, improving performance while reducing cost. Although EB-cured composites have been designed and manufactured for many applications, their performance in the space environment has yet to be determined in detail. Discussions with several experts in the field of satellite design and the use of composites for space applications allowed us to summarize the starting point for grading EB-curable resins for their suitability for space (Table 2).

Table 2: Target Properties/Conditions for Space-Grade Polymers

Selected Target Properties	Target Values
Resin shrinkage	< 5%
Composite void content	< 2%
Total Mass Loss (50% RH initial; composite)	< 1%
Collected Volatile Condensable Materials	< 0.1%
Temperature Range	-100°C to 150°C
Water Uptake	< 3%
Glass Transition Temperature (Tg)	> 200°C (Tan Delta)

Table 3 compares the properties of some of the currently available EB-cured neat resins with 954-2A cyanate ester and 977-3 epoxy polymer (Janke, 1996, 1997). Table 4 provides the available information on selected proprietary EB-curable polymer blends.

TABLE 3: Selected Neat Resin Properties

Selected Polymer Properties	Target Values	954-2A Cyanate Ester	977-3 Epoxy	D-1 EB Resin	D-2 EB Resin	T-1 EB Resin	T-2 EB Resin
Resin Shrinkage, %	< 5%	<5%	~3%	3.5	3.0	3.6	2.5
Glass Trans. Temp (°C)*	> 200°C	215	190	187	246	225	186
Tensile Strength, MPa		68.9	--	44.1	56.3	40.0	35.0
Tensile Modulus, GPa		3.03	--	3.47	3.36	3.70	3.50
Flexural Strength, MPa		117	144.7				
Flexural Modulus, GPa		0.44	3.79	3.26	3.5	3.68	3.03
Water Uptake, %	< 3%	1.28	3.0	1.9	2.1	2.2	2.1
Density, kg/m^3		1240	1200	1210	1220	1202	1198

* Tg based on Tan delta

TABLE 4: Selected Resin Blend Properties

Selected Polymer Properties	Target Values	EB-1	EB-2	EB-3	EB-4	EB-5
Resin Shrinkage, %	< 5%	3.5	4.0	3.4	3.0	3.3
Glass Trans. Temp (^oC)*	> 200^oC	396	393	232	212	212
Water Uptake, %	< 3%	4.90	2.8	2.0	2.90	1.88
Density, kg/m^3		1260	1237	1225	1224	1228

* Tg based on Tan delta

Table 5 shows selected properties of EB-cured composite laminates, along with 977-2 and 977-3 composite properties (Janke, 1996). All five of the EB-cured laminates exceeded the flexural properties of the 977-2 laminates, with four exceeding the flexural properties of the 977-3 laminates. The compression properties for EB-1 laminates are within 3 and 7% of the modulus and strength values, respectively, for the 977-3 laminates. The inter-laminar shear strengths of the EB-cured laminates are about 70-80% of the corresponding values for the 977-2 laminates.

TABLE 5: Property Comparison Of Electron Beam Cured Versus Thermal Cured IM7/Resin (X) Unidirectional Laminates (Data Normalized to 62% fiber volume)

Resin Systems	Fiberite 977-2	Fiberite 977-3	EB-1	EB-2	EB-3	EB-4	EB-5
Cure Conditions	Autoclave Cured (6 h @ 350^oF; 85 psi)	Autoclave Cured (3 h @ 355^oF; 85 psi)	250 kGy	150 kGy	150 kGy	150 kGy	150 kGy
Void Volume, %	Not Reported	Not Reported	1.77	0.72	1.24	0.64	1.18
Tg, ^oC (Tan Delta)	200	190/240	396	392	232	212	212
O^o Flex. Str., MPa	1641	1765	1986	2006	1793	1765	1710
O^o Flex. Mod., GPa	147	150	196	163	163	154	150
O^o Comp. Str., MPa	1580	1680	1565				
O^o Comp., Mod. GPa	152	154	149				
O^o ILSS, MPa	110	127	77	79	79	89	77
Hot/Wet O^o ILSS, MPa		89 (12.9)	61 (8.8)				

*** 1 week. in H_2O @ 160^oF, tested @ 220^oF**

Table 6 summarizes the effects of thermal cycling on the properties of selected EB-cured composite panels. Each of the EB-cured composite products had void contents of less than the maximum allowed value of 2%. The multiple transition temperatures for some of the samples is the result of the specific additives used in the formulations.

Void Content

Void content and laminate consolidation is a major evaluation area EB curing. Initial evaluations have shown that there is considerable promise in achieving the desired 1-2% void content within a complex structure, and that methodologies are available to produce acceptable compaction in composite structures. Consolidation parameters were established for cationic resins prior to fabrication of demonstration hardware (Sidwell, 1997). In order to take advantage of the nature of EB materials, additional optimization would refine the process as the resin systems mature.

Process inspection after consolidation and prior to the EB curing would offer a unique approach to quality control management of composite structures.

Table 6: Electron-Cured Graphite Composite Panels[1]

Property	EB-6	EB-7	EB-8	EB-9	EB-10	EB-11	EB-12	EB-13
Service Temperature, °C [2]	197	185	344	304	212	204	365	365
Glass Transition Temp., °C (Tan d)	202	137/195	435	232	157/420	210	128/435	144/435
Resin Viscosity, poises, @ 70°C	108	114	102	102	74.5	270	223	231
Flexural Strength, MPa	1158	1190	1293	1307	1330	1031	1107	1069
Flexural Modulus, GPa	143	159	148	144	146	143	144	145
Flexural Strength, MPa (cycled) [2]	1169	1244	1400	1272	1317	1083	1228	1166
Flexural Modulus, GPa (cycled) [2]	144	156	145	139	147	147	142	140
Interlaminar Shear Strength, MPa	47.3	50.0	47.6	71.4	71.7	52.4	42.7	39.3
ILSS, MPa (cycled) [3]	59.3	58.3	54.2	72.4	75.5	58.6	50.4	46.6

1. Panels consisted of IM7 Graphite fiber with GP sizing, 12K tow, laid up to thickness of 0.080 inches and debulked at 70°C for 1 hour. The panels were cured using the I10/1 electron accelerator to a dose of 150 kGy.
2. Service Temperature: temperature at which the DMA modulus is at 50% of its room temperature value.
3. Cycling procedure: Composite placed in liquid nitrogen (-194°C) for 30 minutes, returned to room temperature for 30 min, heated at 121°C for 30 minutes, then returned to room temperature for 30 minutes. The panels were cycled three times.

Out-Gassing

Total mass loss was determined according to ASTM procedures, on a series of the most promising EB-cured epoxies resins (resins listed in Tables 4 & 5). Each of the EB-cured samples met the required release limits of 1% (TML) and were slightly above the 0.1% for volatile condensables (CVCM). Table 7 summarizes the complete results of the out-gassing tests to determine the total mass losses and amounts of collected volatile condensable materials in selected composite samples (50% relative humidity), as specified in ASTM E595.

TABLE 7: Out-Gassing of Selected EB-Cured Composites

Selected Properties	RS-3 Cyanate Ester	EB-1	EB-2	EB-4	EB-5
Total Mass Loss, %	0.12	0.27	0.13	0.23	0.30
CVCM, %	0.06	0.13	0.15	0.14	0.10

Effect of Varying Cure Temperature

Internal stresses are induced in multi-directional composites by two processes; resin shrinkage during curing and contraction during cooling. These factors often combine to warp composite products. The stresses induced during cooling can develop within layers, as a result of the low linear thermal expansion of the fibers compared with the resin, or between layers because of the difference in thermal expansion perpendicular to and parallel to the fibers. The composite temperature during EB curing is a processing variable, thus reducing the expected internal stresses.

Figure 1: Effect of Controlled Curing Temperature on Initial Internal Stress (0^oC; 3K Resin; IM-7, 2-ply)

Figures 1 and 2 illustrate the typical effect of curing at different temperatures on the residual stresses within a composite. Residual stresses are related to the measured curvature of the composite strips (Favre, 1985). The panels cured at 0^oC and 25^oC showed very little curvature. The panels cured at 115^oC and 69^oC showed significant curvatures.

Table 8 summarizes how varying the cure temperature effects the initial internal stresses in an EB-cured graphite composite (2-ply; EB-5 resin; IM-7 unidirectional fiber; 50% relative humidity), along with the effect of thermal cycling. Each of the samples was also examined microscopically and by mercury intrusion to determine if micro-cracking was evident. No surface cracking or crazing was observed microscopically. The thermal cycling test showed that varying the cure temperature dramatically affects the initial part distortions due to thermal mismatch of materials, but the products should be expected to behave similarly after a small number of thermal cycles.

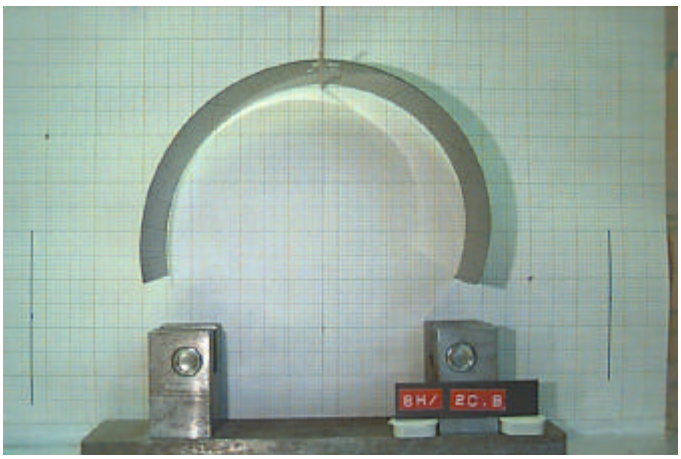


Figure 2: Effect of Controlled Curing Temperature on Initial Internal Stress (115^oC; 3K Resin; IM-7, 2-ply)

Value of EB Curing

AECL staff designed a facility suitable for curing large composite structures. The capital cost of the facility was estimated to be $4 to $5 Million, not including the unique product handling equipment needed for EB curing. The annual operating costs was about $1.5 Million. The overall curing cost was less than $1.00 per kilogram, assuming adequate facility utilization (50%). Although only an estimate, this cost is very low in comparison to the typical

fly-away costs for space products ($2000-$20,000/kg). If an EB curing facility was used at only 10% of its capacity, a conservative assumption, the curing costs would still be below $3.00/kg.

TABLE 8: Effect of Cure Temperature on Initial Internal Stress in EB-Cured Graphite Composite(EB-5 Resin; IM-7, 2-ply laminate; 50% relative humidity)

Selected Properties	*115°C Cure*	*69°C Cure*	*25°C Cure*	*0°C Cure*
Initial Radius, mm @ 25°C	107	141	311	**
Radius After One Cycle, mm	102	111	93	206
Radius After Five Cycles, mm	100	88	86	128
Normalized Stress, after 0 cycles, % *	291	221	100	**
Normalized Stress, after 1 cycle, % *	91	84	100	45
Normalized Stress, after 5 cycles, % *	86	98	100	67

* Normalized to 25°C cured sample ** Sample was flat; infinite radius

As EB curing of composite materials becomes established as an industrial process, there will be far reaching benefits to the entire composites industry, primarily because of reduction in manufacturing costs. Six independent economic studies of the EB curing process in aerospace manufacturing applications, have concluded that cost savings of 25 to 65% are possible. These impressive savings result from the following characteristics of the EB process:

- Curing time is reduced.
- Tooling costs are reduced.
- Unique products may be manufactured.
- Resin stability at ambient temperatures is improved.
- The production of volatiles is minimized.

Estimating the "value" of any technology is not a simple task, and EB curing is no exception. A complete evaluation requires a team approach with the product designers, production managers, material suppliers, EB curing experts, and the end-users all participating. Each team member is key in providing a piece of the puzzle to estimate the true "value" of EB technology for manufacturing space structures.

Summary

EB curing has and will continue to have a growing presence in the aerospace industry, particularly as the technical benefits are more widely understood, and exploited by designers. Over the next five years, the true "value" of EB curing will not be in replacing autoclaves for manufacturing existing composite products to lower production costs but to be able to make unique products to meet the ever increasing demands of the aerospace industry.

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