Abstract

Electron beam curing of fiber reinforced composites was explored over thirty years ago. Since then there have been developments in accelerator technology, in processes for handling materials presented to an accelerator, and in materials that can be used as matrix binders. In recent years in North America, Cooperative Research and Development Agreements (CRADAs) have been formed involving collaboration amongst materials suppliers, accelerator manufacturers and service providers, national laboratories, such as Oak Ridge National Laboratory (ORNL), and interested potential users. The scope and status of these CRADAs are reviewed along with other recent developments in the electron beam curing of composites in North America. Innovative and proprietary materials technology has been developed and progress made toward implementing commercial practice. Significant market interest has developed in the
military/aerospace industries that are finding the process and performance of electron beam cured composites to offer significant benefits.

Introduction

The use of ionizing radiation from an electron beam or from x-rays generated by such beam offers many compelling advantages in the curing of polymer matrix fiber composites when compared with more traditional thermal curing techniques. Electron beam curing is fast, energy efficient, environmentally friendly, safe, and offers considerable control and some process latitude in contrast to thermal curing techniques. A number of papers have documented these advantages as has the evolution of the electron beam curing of composites since the mid-1960s.\(^{(1)(2)(3)(4)}\) Current interest in electron beam curing of composites is sufficiently high such that there is a popular full-day technical session on this topic at the annual Society for the Advancement of Material and Process Engineering (SAMPE) Symposium and Exhibition. ORNL has hosted four multi-day workshops since 1996, averaging over one hundred attendees, and there was a workshop for Canadian institutions last year in Winnipeg, Manitoba.

Two factors have contributed to the growing interest in the electron beam curing of composites:

1. The development of high current, commercially industrial accelerators capable of attaining the high beam penetration of 10 MeV.
2. The development of radiation responsive oligomers, initiators and formulation systems tailored for the needs of composite matrices.

Structural, fiber-reinforced polymer composites are typically a few millimeters to more than a centimeter thick. Therefore, accelerator voltages of $\geq 3$ MeV are needed to penetrate both tooling and to cure practical composite structures. A typical carbon fiber composite structure with a 1.6 g/cm$^3$ density can be penetrated with 10 MeV electrons with equal entrance – equal exit dose to approximately 2.0 cm, which would be a rather thick structural part.

The resins or oligomers designed for radiation curable response do not typically have to meet the demands of the higher performance resins required by aircraft and aerospace applications. Typical radiation curable oligomers are often tailored for decorative uses as in inks and coatings. In cooperation with oligomer suppliers, Aerospatiale developed the first practical application of electron beam cured structural composites for solid rocket motors using acrylated epoxy resins.$^{(5)(6)}$ As shown in Figure 1, these resins produced composites that were quite satisfactory for the structural rigidity called for in this application. However, these materials were found to be too brittle for manned and reusable aerostructures. In the mid-1990s, researchers from ORNL and Atomic Energy Canada, Limited (AECL) found that commercially available epoxy resins could be modified and rendered electron beam curable with the use of specific cationic initiators. At modest dose, properties comparable to those of thermally cured analogs were attained.$^{(7)}$
Interest in the electron beam curing of composites was further stimulated by the realization that this process provides compelling economic advantages over thermal curing. Several independent studies have shown that electron beam curing of composites can offer cost reductions ranging from 10% to well over 50% for the original manufacture of aerostructures, depending on the specific part design and configuration, production volume, and so forth.\textsuperscript{(7)(8)(9)} Acsion Industries and Air Canada have recently demonstrated that the use of electron beam cured composites in commercial aircraft repair applications yields similar cost savings, even before considering improved aircraft
availability. All of the cost studies and manufacturing demonstrations conducted to date on aerostructures have shown cost advantages for electron beam curing in comparison to traditional thermal curing.

Recent Developments

From 1994 to 1997, the U.S. Department of Energy (DOE) sponsored a CRADA in which ORNL, Sandia National Laboratory, and ten industrial partners collaborated. This CRADA resulted in the development of electron beam responsive epoxy resin formulations, as well as a study of tooling materials, and a rigorous economics study. Novel manufacturing scenarios were explored, such as the “lost core” process shown in Figure 2, in which a melt-out wax mandrel was used to form a complex shape.

Figure 2. E-beam cured structure fabricated with “lost core” wax tooling.
Table I shows some of the best properties attained with electron beam curable composites as of 1997.\textsuperscript{(12)}

### Table I. Electron Beam Curable Resin Properties

<table>
<thead>
<tr>
<th>Resin System</th>
<th>977-2\textsuperscript{a}</th>
<th>977-3\textsuperscript{a}</th>
<th>EB 8H</th>
<th>EB 10H</th>
<th>EB 9H</th>
<th>EB 3K</th>
<th>EB 1K</th>
<th>EB 1L</th>
<th>Units</th>
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<tr>
<td>Cure Conditions</td>
<td>6 hrs, 177 °C 85 psi</td>
<td>3 hrs, 180 °C 85 psi</td>
<td>250 kGy</td>
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<td>Void Volume</td>
<td>NR\textsuperscript{b}</td>
<td>NR</td>
<td>1.77</td>
<td>0.72</td>
<td>1.24</td>
<td>0.64</td>
<td>1.18</td>
<td>1.7</td>
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<td>Dry T\textsubscript{g}°</td>
<td>200</td>
<td>190</td>
<td>396</td>
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<td>232</td>
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<td>1765</td>
<td>1986</td>
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<td>1324</td>
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<td>0° ILSS</td>
<td>110</td>
<td>127</td>
<td>77</td>
<td>79</td>
<td>79</td>
<td>89</td>
<td>77</td>
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<td>MPa</td>
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<td>89</td>
<td>61</td>
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The initial electron beam curable composites CRADA accomplished its objective to develop useful new materials. However as other projects began to more intently use and study these materials, it became evident that they were some deficiencies in the interlaminar shear and toughness of composites based on these formulations. Thus, another CRADA was initiated to address these issues. This CRADA is also led by ORNL, under DOE sponsorship, and features many of the same industrial partners, but

\textsuperscript{a} Thermally cured Fiberite resin
\textsuperscript{b} NR = not reported
\textsuperscript{c} T\textsubscript{g}° measured by tan delta method
\textsuperscript{d} Hot-wet specimens conditioned in water, ≥ 71 °C for 7 days or 82 °C for 4 days.
with the crucial addition of two carbon fiber manufacturers.\(^{(13)}\) Work in this second CRADA began in April 1999 and will be completed in April 2002.

Deficiencies in interlaminar shear strength are believed to be the result of poor fiber-matrix adhesion. Studies have shown that the interfacial shear strength, as measured by debonding fibers from the matrix via nanoindentation techniques, is typically 30\% to 60\% lower than that of thermally cured analogs.\(^{(14)}\)(\(^{(15)}\)) Using this methodology, adhesion appears to be minimally affected by irradiation parameters. It should be noted that the available surface treatments on carbon fibers have been developed for thermal curing. Thus it is not surprising that the most promising methods for increasing fiber-matrix adhesion appear to be by modifying the chemistry at the fiber-matrix interface. This approach has already shown several methods for increasing interfacial shear strength by 30\% to 50\%.\(^{(16)}\)

Initially matrix resin toughness was found to be typically about 50\% lower than that of analogous thermally cured resins. However, as illustrated in Figure 3, electron beam curable matrix resin toughness has been improved so that now many of these materials are as tough or tougher than their thermal analogs.\(^{(17)}\)(\(^{(18)}\)) Electron beam curable resin technology is licensed to UCB Chemicals Corporation and Applied Poleramic, Incorporated.

\[^{6}\text{ILSS} = \text{interlaminar shear stress}\]
Other Recent Developments

There have been numerous other noteworthy development programs involving electron beam curable composites in the mid and late 1990s:

♦ Prototypical manufacture of Composite Armored Vehicle side skirts. Vacuum Assisted Resin Transfer Molding was combined with electron beam curing. The low temperature cure minimized distortion attributable to curing multi-layered armor with disparate CTEs, and also allowed the use of wood tooling.\(^{(19)}\) The Army Research
Laboratory (ARL), Science Research Laboratory (SRL), and University of Delaware are continuing to develop resins, adhesives, and processing technology with a focus on US Army combat vehicle needs.\textsuperscript{(20)(21)}

- SRL has also conducted significant work for the U.S. automotive industry using electron beam curing of adhesives to bond automobile structures.\textsuperscript{(19)}

- The US Air Force and its prime contractors are maturing electron beam curing technology for military aircraft in the Composites Affordability Initiative.

- Prototypical manufacture of LONGFOG missile bodies, shown in Figure 4. Electron beam curing allowed the replacement of over 100 kg of castable, melt-out metal tooling by replacing it with very light epoxy/foam and plywood tooling, as well as simplifying the integration of two sections of the structure. Electron beam curing also allowed the use of multiple matrix resins that could be cured in a single pass under the beam.\textsuperscript{(22)}
Figure 4. Electron Beam Irradiation of LongFOG Missile Body

- Prototypical manufacture of a T-38 trainer aircraft windshield frame. The arch was a laminate construction of 36 thin stainless steel strips, with electron beam curable adhesive between the strips. This stainless steel laminate was then overwrapped with fiberglass reinforcement. The frame was electron beam cured; the arch was irradiated using electron beam generated x-rays to ensure curing of the adhesive between the metal strips.\(^{23}\)(\(^{24}\))

- Development of resins and manufacturing processes for three dimensional braided structures for use in aircraft ducting applications.\(^{25}\)

- Electron beam curing has been applied in numerous filament winding applications including flywheels\(^{26}\), tactical rocket motorcases,\(^{27}\) and helicopter drive shafts.
♦ Acision Industries and AirCanada are demonstrating rapid composite repair on commercial aircraft.\textsuperscript{(10)} Fairings have been flight tested for hundreds of cycles and well over a thousand flying hours with good results.

♦ The U.S. National Aeronautics and Space Administration (NASA) is investigating electron beam curing technology for application in the curing of composites to be used in cryogenic piping, tanks, and as repair pieces of space structures under its Advanced Space Transportation Program.\textsuperscript{(28)(29)} NASA also successfully fabricated a scaled prototype of an overwrapped FASTRAC rocket nozzle, in which material temperatures were held low to eliminate delamination attributable to high thermal stresses.

♦ NASA and subcontractors have been investigating the electron beam curing for polyimides.\textsuperscript{(30)} To date, there have been no announced breakthroughs, but there has been encouraging progress toward understanding and resolving the barriers.

♦ Cure monitoring is beginning to receive attention. Scintillating dosimeters are under development.\textsuperscript{(31)} Non-contact cure monitoring/dosimetry methods have also been proposed.

♦ Cure kinetics are being investigated in greater detail. Palmese et. al. have shown that the type and concentration of hydroxyl-containing materials in matrix resins influences the reaction mechanism and can depress the cured material’s glass transition, Tg.\textsuperscript{(32)} Vorobyev and Korenev\textsuperscript{(33)}, and other investigators, are characterizing monomer conversion rates. Dabestani et. al. are investigating the effects of dose rate on the matrix curing reactions.\textsuperscript{(34)}
New electron beam irradiation facilities are emerging with emphasis on composites technology. A laboratory dedicated to electron beam curing and operated by the University of Dayton Research Institute was commissioned in 2000. NASA has a low voltage electron beam “cure-on-the-fly” capability under development. Kent State University recently commissioned a 5 MeV, 150 kW Dynamitron.

Conclusion

A multiplicity of innovative end-uses for electron beam curable composites are in the prototype stage in North America. Electron beam curable matrix resins have been found to be comparable in most aspects to traditional thermally cured systems. However, with the electron beam curing process, economic studies have shown that the near instantaneous cure and use of environmentally friendly chemistry can lead to considerable cost savings in composite manufacture. Beyond the consideration of large structures, there has been significant development in the methods of component and part manufacture that now makes electron beam curing more amenable for use with components of modest size.

Aircraft and aerospace end users are presently driving the technology. However, automotive manufacturers are beginning to make inquiries. Small projects exploring the technology’s applicability to automotive or Commercial Heavy Duty Vehicle manufacturing are likely to commence within the next year.
An increasing diversity of facilities capable of doing development and even production work on electron beam curable composites is emerging in North America. All of this bodes well for the eventual commercial acceptance of this efficient curing and manufacturing process.

Acknowledgements

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References

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