

ELECTRON BEAM PROCESSING FOR AUTOMOTIVE COMPOSITE APPLICATIONS

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Abstract

Electron beam (EB) processing has been used for many years to modify polymers for a number of important industrial applications. More recently, a significant amount of research and development effort has been directed at electron beam curing of advanced composites, primarily for aerospace applications.

An overview of potential uses of this technology for automotive applications, including curing of SMC and RTM /VARTM components, filament wound components, large body/chassis components, adhesive bonding of composite components, composite resins, and thermoplastic composites, as well as some important non-composite automotive applications, is presented.

1. Introduction

High energy electrons may be used to modify polymer materials through direct electron-to-electron interaction. When electrons of sufficient energy interact with a polymeric material, they can create active species such as free radicals. There are three possible outcomes: cross-linking, degradation or grafting. Each of these can offer potential benefits or bring about drawbacks on the properties of the polymer, depending on the application of the polymer and the specific processing conditions used. If the processing conditions are chosen judiciously, important property enhancements can be gained.

Cross-linking: Forms a network among the polymer chains and increases the molecular weight; improves temperature resistance, chemical resistance, and mechanical properties.

Degradation: Reduces the molecular weight by chain scission; adjusts melt flow properties; enables the production of fine powders of certain polymers.

Grafting: Polymerizes a monomer onto the polymer chain; modifies the surface properties of a polymer substrate; introduces new functionalities.

High energy electrons can also initiate polymerization of a monomer or an oligomer and impart the properties of a polymer to the material.

The high energy electrons (generally 300 keV to 12 MeV) are generated by electron beam accelerators. These machines can produce powerful beams capable of processing large quantities of polymers, often in excess of several tons per hour.

An important variable for electron beam processing is the dose delivered. Dose is defined as energy absorbed per unit mass and is expressed in kiloGray (kGy), where one Gray is defined as one joule per kg. The dose must be high enough to cause the desired effect (the minimum dose), yet not so high as to cause any other undesired effects (the maximum dose).

The depth of penetration for the energy deposition is determined by the beam energy of the accelerator and the density and geometry of the material being processed. For a reasonably uniform dose distribution, a 10 MeV accelerator is generally capable of delivering its dose to a depth of about 3 to 3.5 cm in a unit density material, and to 2.4 times that depth if the product may be treated from two sides.

The processing rate is proportional to the power of the accelerator. As an example, an accelerator rated at 10 MeV and 200 kW (such as the Rhodotron[®] manufactured by IBA) is capable of processing up to 4 tons/hour to a minimum dose of 100 kGy. Although the capital cost of accelerators can range from a few hundred thousand dollars to several million dollars, this high throughput rate can result in polymer processing costs as low as a few cents per kg. It is not necessary for a user to own and operate the accelerator facility themselves. Several companies around the world offer toll-processing services.

Today, there are hundreds of industrial accelerators in operation around the world, the large majority of which are dedicated to polymer processing on an industrial scale. Some of the most common polymer applications are:

- Wire and cable cross-linking
- Production of PTFE micropowders
- Heat-shrinkable connectors and films
- Manufacturing of cross-linked PE pipe and tubing (PEX)
- Vulcanization of synthetic and natural rubbers and latexes
- Cross-linking of closed-cell foams
- Property enhancement for gaskets and o-rings through cross-linking
- Bulk polymer modification by pre-treatment of pelletized resins prior to forming

2. Benefits of EB Processing

The widespread use of electron beam processing of polymers comes from a number of fundamental advantages of this technology. The energy is delivered directly to the molecules, thus there is no need to heat the material in ovens or tools, or to allow for permeation of chemicals into the material being processed. For cross-linking, there are usually no residues or by-products. Since the process occurs without heat, there may be no need for strict temperature control. (Heat may be produced either by an exothermal reaction or as a result of direct conversion from the dose absorption. In some cases, temperature increases might need to be offset.) The cross-linking, degradation, grafting or polymerization is usually complete immediately after processing. The process is highly reproducible, controllable and precise because electron beams can be well controlled by setting the parameters of the accelerator. All of these benefits can often add up to significant cost savings for the polymer product producer.

3. EB Curing Of Composite Materials

In recent years, a great deal of research and development activity has been expended on the use of EB technology for the curing of advanced composites for the aerospace industry. Curing involves the polymerization of monomers or oligomers and cross-linking of polymers. EB curing offers the following important benefits:

- Ambient temperature curing
- Less stress caused by temperature differences
- Co-curing of dissimilar materials
- Simplified tooling
- Improved material properties
- Easier material handling
- Precise control
- Lower processing cost

Table 1 shows a comparison of some typical properties of EB cured and thermally cured resins for composites^{1,2}.

Table 1: EB Cured and Thermally Cured Resin Properties

Property	EB Cured (150-250 kGy)	Thermally Cured (3hrs/180 °C/85psi)
Void Volume (%)	0.6-1.7	ND
T _g (°C, tanδ)	210-390	190-240
Water Uptake (%)	1.8-4.9	ND
Resin Shrinkage (%)	3.0-4.0	ND
Density (g/cm ³)	1.22-1.26	ND
0° Tensile Strength (MPa)	1870-2260	2510
0° Tensile Modulus (GPa)	157-168	162
0° Compressive Strength (MPa)	1430-1680	1680
0° Compressive Modulus (GPa)	149	154
0° Flexural Strength (MPa)	1710-2006	1765
0° Flexural Modulus (GPa)	150-196	150
0° Interlaminar Shear Strength (MPa)	127	77-89

ND = no data

For the automotive industry, the application of the fundamental benefits of EB curing can be different for different products and processes.

SMC and RTM/VARTM components. Resins capable of SMC and RTM/VARTM processing for composite materials have been designed to allow an initial B-stage cure in simplified (non-metal) tooling at room temperature, followed by a final rapid EB cure outside of the tool³. Components constructed of dissimilar materials may be cured in this manner, including those composed of metals and polymers, since differential thermal expansion may be limited due to the ambient temperature nature of the cure. It has been shown that curing of RTM automotive parts using this process is cost-effective, especially at low production volumes⁴. Investigations are also underway to demonstrate the capability to cure PMC automotive panels at high production volumes, with a goal to demonstrate superior quality and lower cost than conventional SMC methods⁵.

Filament wound components. Table 2 lists some of the properties for EB cured and thermally cured filament-wound laminates¹.

Table 2: EB Cured and Thermally Cured Filament-Wound Laminate Properties

Property	EB Cured (150kGy)	Thermally Cured (3hrs/121 °C +3hrs/150 °C+4hrs/177 °C)
T _g (°C, tanδ)	192	218
0° Tensile Strength (MPa)	2358	1986
90° Flexural Strength (MPa)	70	68
0° Interlaminar Shear Strength (MPa)	74	57

An EB facility has been established in France specifically designed for the curing of filament-wound rocket motor cases⁶. The same concepts can be applied to curing filament- or tape-wound automotive structural components or pressure vessels for alternate automotive fuels. It has been postulated that using ambient temperature curing will reduce micro-cracking in an EB cured pressure vessel which should lead to improved resistance to gas/VOC permeation. This resistance may be further enhanced through incorporating polyethylene liners that are cross-linked concurrent with the vessel curing and/or incorporating EB-grafted monomers onto the surface of the PE liner.

Large body/chassis components. Large laid-up or tape-wound composite monocoque or other body/chassis components may be EB cured in one operation. EB curing makes it possible to incorporate multiple polymer or metallic materials, and cure them in one operation. As a result, the process has

reduced curing time and potentially a reduced number of processing steps in the operation. This has the potential of offering significant curing cost savings.

Adhesive bonding. Adhesive bonding of thick composite or polymer panels may be cured rapidly at ambient temperature using special EB-curable materials. Advantages include fewer processing steps, reduced cost and elimination of autoclave/oven processing, reduced residual stress and prevention of debonding of dissimilar materials.⁷ The process may be accomplished using one-component paste adhesives, two-component paste adhesives, and film adhesives. A dual curing method may be employed, with thermal polymerization of conventional condensation chemistry (at room temperature to 60 degree C) plus EB curing via free radical or cationic mechanisms. The resulting IPN (interpenetration network) yields very high lap shear strength³.

Composite resins. Resins composed of a polyolefin compounded with a chopped fiber may be pre-processed at a low dose for a low degree of cross-linking to enhance molding or final part properties.

Thermoplastic composites. A fully formed thermoplastic composite part may be later cross-linked to produce a thermoset composite. EB post-curing has the cost advantages of a thermoplastic and enables conventional fusion bonding among different parts (which is not possible for thermoset composites).⁸

Materials and tooling. The EB curable resins remain stable at ambient temperature, and therefore have potentially unlimited shelf life. This not only reduces costs through reduced scrap, but also allows for easier clean up. Also, since the curing process occurs at ambient temperature, tooling materials may be constructed from a wide range of low-cost materials, such as wood, wax, Styrofoam or cardboard tubes.

4. EB Processing of Other Polymer Materials for Automotive Applications

In addition to composite materials, EB processing offers many advantages for other automotive materials applications.

Formed thermoplastic components may be cross-linked to significantly improve thermal stability, mechanical properties and other important characteristics. This may be particularly advantageous for under-hood components that are exposed to high temperatures. This may allow the replacement of certain under-hood metal or higher cost polymer components with cross-linked, low cost polyolefin materials.

VOC permeation improvement for automotive fuel system components may be achieved through cross-linking of PE or other fuel system component materials⁹. It may also be enhanced by EB-grafting a selected monomer onto the surface of the polymer substrate. Cross-linking will reduce polymer chain mobility and free volume, have a higher chemical resistance, exhibit less swelling, and generally offer an improved penetration barrier to the fuel. EB grafting of certain polar or other monomers onto a polyolefin substrate should enhance repellence of VOCs and improve chemical resistance, and may also form a dense layer that should help block permeation resistance. These cross-linking and grafting methods may be combined in one EB processing operation, and the net result should be significantly improved VOC permeation resistance. Grafting may also be employed to impart unique surface properties to a wide range of automotive components.

Paints and coatings may be very rapidly cured with EB. In fact, UV and EB curing of paints and coatings for automotive and other industrial applications have been used on a large scale for many years. With high energy, high power EB accelerators that have X-ray conversion capability today, it may now be possible to very rapidly cure through entire, large automotive components, including all sides of complete body frames. Moreover, EB curing will allow the paints or coatings on temperature sensitive panels (such as thermoplastic ones) to be rapidly cured without fear of heat-related side effects on the panels. This would allow the potential to cure several layers of paints and coatings on a component with minimal time between the application of each layer.

X-ray Capabilities. Curing of large parts or complex geometry may require converting the electron beam to X-rays which are far more penetrating¹⁰. This may be possible for the first time with the recent

introduction of very high power accelerators. A very high power beam will be able to provide a sufficiently high processing rate for X-ray processing. Curing of different composite parts and paints or coatings can all take advantage of the benefit of the much deeper penetration of X-rays. In fact, a process can be envisaged whereby a composite material, its adhesives and its paints or coatings are all cured in one operation⁴.

5. Conclusions

EB technology has been demonstrated over the past few decades to be a cost-effective means of modifying a wide range of polymers for a variety of industrial applications. This is a result of a number of fundamental and unique advantages that are inherent to this technology. Many of these advantages can be successfully applied to improve the quality and reduce the cost for a wide range of composite and other related automotive materials applications. The recent advances in the range of energy and power levels of industrial accelerators, and the ability to convert electron beams to high energy X-rays, make some of these applications feasible for the first time.

6. References

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