ASSESSMENT OF ELECTRON BEAM AND X-RAY CURE ADHESIVES FOR COMPOSITE REPAIR

Tamunoiyala S. Koko, Mirko Zgela, and Kenneth D. MacKay

Martec Limited, 1888 Brunswick Street, Suite 400, Halifax, NS, Canada, B3J 3J8

SUMMARY: This paper presents a study to evaluate electron beam (EB) and X-ray curable adhesives that could be used for composite repair of aircraft structures. A review of EB/X-ray technology as it relates to composite structural applications was first performed to assess potential adhesive systems for the application. Two candidate adhesive systems were tested in single lap shear configuration and their mechanical properties were compared to thermally cured adhesives currently being used for composite repair of aircraft structures. The shear strengths of the EB adhesives ranged from 14 to 21 MPa compared to 32 to 35 MPa for the thermally adhesives, and the EB adhesives exhibited more brittle behavior.

KEYWORDS: electron beam, x-ray, adhesives, composites repair, aircraft structures, graphite epoxy, single lap shear tests.

INTRODUCTION

Adhesive bonded composite joints and repairs are increasingly being used for high performance structures in the aerospace, civil and marine industries. Their use results in lighter weight, smoother skin surfaces, higher fatigue resistance and lower fabrication costs. [1]. In these applications the adhesives are typically cured by heating for several hours in large autoclaves, presses or heat blankets. This results in high processing costs in terms of equipment and labor costs. In addition, the use of high temperature adhesive curing causes thermal residual stresses to build up in the components that are bonded together due to differences in their coefficients of thermal expansion. These stresses tend to weaken the adhesive bond and increase its susceptibility to stress-corrosion. All of these factors tend to limit the performance of high temperature cured adhesive joints and repairs.

Electron beams (EB) and X-rays, which have the ability to deposit large amounts of energy on the substrates, offer significantly attractive features for adhesive curing. The most attractive feature is that with electron beams and X-rays as sources of energy, curing can be achieved at ambient temperatures and contact pressure in very short time periods. As a result residual thermal stresses which usually accompany high temperature curing can be eliminated, thereby ensuring longer life of adhesive bonded components. Other benefits of electron beam and X-ray curing include simplified processing methods, higher energy efficiency due to the elimination of autoclaves and heat blankets, better shelf life of electron beam curable adhesives, and environmental friendliness due to low volatile emissions. Because of these advantages, a number of efforts have been made in the present decade to apply the EB and X-rays for the manufacture and repair of advanced composites [2-15]. Table 1 compares the properties of EB adhesives with thermally cured ones.

This paper provides a study to investigate the applicability of EB and X-ray curing adhesives for composite patch repair of metallic structural components. The thrust of the study was to evaluate EB and X-ray adhesives that can be used as replacement materials for the thermally cured FM73 and FM300-2 materials that are frequently used for composite repair of aircraft structures. The remainder of this paper is organized as follows. In the next section, a review of electron bean and X-ray technology as it relates to composites structural applications is provided. The review covers processing, material systems, applications and activities on the technology in North America. The experimental investigations are then described with the results discussed thereafter. The paper ends with a summary and conclusions.

REVIEW OF ELECTRON BEAM AND X-RAY ADHESIVE CURING

A detailed review of EB/X-ray curing of adhesives was performed by the authors [11] to assess the state of the art of the technology. A summary of the review is presented in this section.

Description of EB and X-Ray Curing

All matter is made up of atoms, which consist of three elementary particles: (i) protons with positive charges; (ii) neutrons with no charges; and (iii) electrons with negative charges. The protons and neutrons form the nucleus and the electrons, which are much lighter orbit around the nucleus. The electrons are so loosely attracted to the nucleus that they are relatively easy to separate from the atom. When energy is applied to a material with loosely bound electrons, a stream of electrons is released. An electron beam is formed when the stream of electrons is focussed into a well-defined beam. On the other hand, x-rays are formed when an electron beam bombards a heavy metal such as tungsten or tantalum. X-rays are electromagnetic waves which have shorter wavelength ($< 10^{-8}$ m) than ultra-violet (UV) waves. When the wavelengths of the x-rays are less than 10^{-11} m, they are often referred to as gamma rays.

The EB and x-ray technologies have been around for over five decades and have been used for a variety of applications in the medical, chemical, physical, biological and electronic fields. Recently, there is a renewed interest in EB and x-ray technologies for curing of structural adhesives for composites fabrication and composites repair. For this application, high-energy electrons and/or x-rays from an accelerator are used to initiate polymerization and cross-linking reactions at controlled dose rates in the structural adhesives [2-4].

Processing and Equipment Requirements

Accelerators are used to produce beams of high velocity electrons that are directed at the component. Figure 1 shows a typical accelerator. The electrons are produced by heating a wire filament in an evacuated chamber (called an electron gun) to form a cloud of electrons. To achieve greater electron speeds, the electrons are run through a series of accelerating chambers. As the electrons move from one chamber to the other, more force is applied to them and they move with increasing speed. At the end of the chambers they pass through a magnet which causes them to form a beam that moves over the components to be cured.

The distance the electrons can penetrate depends on their energy (given by electron charge e, $\times$ electric potential, V and expressed in electron volts (eV)); and by the density of the material. The effective beam penetration for relatively uniform dosage, can be estimated from the following equation:

$$W_a = E/2.2 \tag{1}$$

where W_a is the material areal weight in g/cm^2 and E is the beam energy in MeV [3]. Thus the penetration for a material of density ρ(g/cm^3) is given by $t = W_a/\rho$. An important parameter in EB processing is the minimum dosage required for complete curing the adhesive. This would ensure that small increases in material thickness above the deposition limit could be compensated for by additional exposure. The dosage is measured in unit of kGy (=1000 J/Kg or kilo Gray). When greater penetration is required, the electron beams (EB) are converted to x-rays by bombarding the EB on a heavy metal such as tungsten or tantalum, resulting in an order of magnitude increase in penetration depth. Although EB curing is not a thermally driven process, some heat energy is generated during the process [3].

Accelerators are classified, according to their energy levels, into three categories – low (0-1 MeV), medium (1-5 MeV) and high (5-12 MeV) energy accelerators. The low energy accelerators are suitable for surface curing and the medium and high level accelerators are suitable for deeper penetration of products. Accelerators are available either in the form of fixed installations or as portable equipment at several institutions in North America, including:

- Atomic Energy of Canada Limited (AECL) [4,5];
- E-Beam Services, Cranbury, NJ [6];
- Radiation Dynamics, Inc., Plainview, LI, NY [2];
- Irradiation Industries Incorporated, Gaithersburg, Maryland [7]; and
- Schonberg Research Corporation, Santa Clara, CA [8,9].

EB/X-Ray Adhesive Material Systems and Formulations

The major attractive features of electron curable adhesive systems are that they can be cross-linked at ambient temperatures, and the cross-linking can be controlled, which makes the process attractive for high-speed operations. In general, an electron-curable adhesive system consists of one or more oligomeric resins (compounds of relatively low molecular weights containing up to five monomer units) or prepolymers, together with additives such as plasticizers, diluents and wetting agents [10]. The most common EB/X-ray resins are principally acrylates and epoxies. The electron beam curable adhesives are also categorized as either free radical or cationic, according to their curing mechanisms. The free radical curing adhesives are the most commonly used resins, such as acrylates. The disadvantage of these systems is that oxygen inhibits the curing mechanism, which may result in tacky and incompletely cured material. On the other hand, the cationic curing resins are generally epoxybased resins in which oxygen does not interfere with the polymerization or curing process, and the resins have considerably lower shrinkage than the free radical curing acrylates. Adhesive systems, which have shown promise, include [11]:

- Epocryl 12 from Shell Chemical Co., Houston, Texas;
- Loctite 306, 312, 317 and X-353 from Loctite Corporation, Newington, CT
- Acrylated epoxies (EA1, CN104, FW3)
- A modified bismaleimide (BM11)
- AECL proprietary resins

Applications and Activities on EB and X-Ray Composites Technology

Several studies on the use of electron beam and x-ray curable resins for fabrication of composite materials and for composites repair have been reported in the literature. These are discussed in detail in [11]. A good number of these studies have focused on characterizing EB/x-ray resins for fabrication of composites. However, a few practical applications of EB cured composite components have also been reported. Some of the significant studies are discussed below.

Saunders et al [12] of AECL have investigated EB curable adhesives for fabrication of thick composites as an alternative to thermal curing. Two commercially available EB resins, an acrylated epoxy (EA1) and a modified bismaleimide (BMI1) were used to fabricate carbon fiber reinforced composites and evaluated. Janke [13] also reported on the application of several toughened EB adhesives for composites fabrication. In these studies, the properties of the EB cured materials were comparable to their thermally cured counterparts. The Oak Ridge Center for Manufacturing Technology (ORCMT) has assisted several US companies to develop electron-beam-cured composites for advanced structural applications (see [11]). Researchers at AECL [14] have also considered EB adhesive composite repair of structures.

Most of the activities on EB/X-ray composites technology, in North America, are centered around key organizations that are either performing their own investigations or providing support to smaller organizations participating in EB/x-ray technology. Significant organizations include:

- The Atomic Energy Canada Limited (AECL);
- A Cooperative Research and Development Agreement (CRADA) sponsored by the Department of Energy and 10 industrial partners in the USA; and
- The Oak Ridge Center for Composites Manufacturing (ORCMT).

EXPERIMENTAL PROGRAM

Following an initial screening exercise, two adhesives designated as 11L and 16L were obtained for further study. These are toughened cationic epoxy formulations that are proprietary to the Atomic Energy Canada Limited (AECL). In order to evaluate the mechanical properties of the adhesives, single lap shear (SLS) coupons were prepared using AS4/3501-6 laminates. The coupons were obtained from laminates that were manufactured from 12 unidirectional plies of AS4/3501-6 pre-preg material. Surface preparation involved light sanding followed by cleaning with an adhesive tape. The SLS adhesive joints were EB and X-ray cured at AECL's facilities in Pinawa, Manitoba, Canada. Table 2 presents the test matrix, highlighting the various EB and X-ray doses that were applied to cure the samples. Five samples were used for each set of tests, in order to provide good statistical averages. The shear strengths and shear moduli of the EB/X-ray adhesives are presented in Figure 1 along with the corresponding values for the thermally cured FM73 and FM300-2 adhesives that are commonly used for composite patch repair. The shear strengths of the EB/X-ray adhesives are generally lower than those of the thermal cured adhesives, whereas their shear moduli are higher. How the EB/X-ray adhesives compare against the thermal cure adhesives in a typical repair design is discussed in the paper.

RESULTS AND DISCUSSIONS

The properties of the two adhesives were obtained by averaging the results from the five samples for each test case. The tests were very repeatable in most cases. However, results from two bad samples were ignored to avoid their effect on the results. Table 3 provides a summary of the results of the study. The mean shear strengths of the 11L material ranged from 13.9 MPa (2013.4 psi) to 15.5 MPa (2243.8 psi), whereas those for the 16L material ranged from 14.7 MPa (2132.2 psi) to 21.2 MPa (3070.3 psi). It is instructive to note that the room temperature shear strengths of the thermally cured adhesives FM73 and FM300-2 that are traditionally used for composite repairs are 35.5 MPa (5150 psi) and 32.1 MPa (4656 psi), respectively. These are also shown graphically in Figure 1. From these results it is seen that the shear strengths of the electron beam adhesives are lower than those of the thermally cured adhesives. However, as the figure shows, the electron beam cured adhesives have higher shear moduli than the thermally cured adhesives. The maximum shear moduli of 11L and 16L are 5.77 GPa (836.9 ksi) and 5.00 GPa (725.2 ksi), respectively, whereas the corresponding values for FM73 and FM300-2 are 0.36 GPa (52.2 ksi) and 0.57 Gpa (82.7 ksi), respectively.

The effect of electron dose on the behaviour of the 11L and 16L adhesives is shown in Figure 2. For the 11L material, the use of 75 kGy to 150 kGy of electron beam or 150 kGy of X-rays does not have any significant effect on the shear strength. The maximum shear strength for the material was obtained when the dose was 100 kGy. For the 16L material the maximum shear strength was obtained when the adhesive was cured by 150 kGy dose of electrons. The shear strengths at other doses were also fairly uniform, although they were somewhat lower than for the 150 kGy-cured sample. However, these results show that the adhesives were adequately cured and also did not degrade as a result of using higher electron doses.

The electron beam and X-ray cured adhesives showed very brittle behaviour with very low failure strains. The elastic shear strain limit for 11L ranged from 0.0026 to 0.0035 and those for 16L ranged from 0.0038 to 0.0052. Figures 3 and 4 show typical shear stress-shear strain curves for the 11L and 16L adhesives. The figures show that the adhesives exhibit marginal plastic behaviour beyond the elastic limit. Consequently, the failure strains (maximum shear strains) of the electron beam cured materials are only marginally higher than the elastic shear strains. This is in contrast with thermally cured adhesives, which exhibit considerable plastic behaviour.

SUMMARY AND CONCLUSIONS

This report provided a description of experimental investigations on the behaviour of two candidate electron beam adhesives for composites. The two materials are AECL's adhesives designated as 11L and 16L. The room temperature shear strengths properties of the electron beam adhesive ranged from 14 to 21 MPa compared to 32 to 35 MPa for thermally cured adhesive. However, the electron beam adhesives had much higher shear moduli than the thermal adhesives. Furthermore, the 11L and 16L materials exhibited brittle failure with failure strains as low as 0.4 %. These factors must be taken into account in designing composite repairs that utilize these adhesives.

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Table 1: Key Features of EB-Curable Epoxy Resins [15]

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 20ºC	Limited lifetime below 0ºC
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 ©	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)

Table 2: Test matrix for evaluation of properties of EB/X-ray curable adhesives

TEST	SUBSTRATES	ADHESIVE	CURE

DESIGNATION			CONDITION
C-75-11L	AS4/3501-6 on	11L	75 kGy EB
C-100-11L	AS4/3501-6	11L	100 kGy EB
C-150-11L	(1.625 mm thick)	11L	150 kGy EB
C-XR-11L		11L	150 kGy X-ray
C-75-16L		16L	75 kGy EB
C-100-16L		16L	100 kGy EB
C-150-16L		16L	150 kGy EB
C-XR-16L		16L	150 kGy X-ray

Table 3: Summary of experimental results

TEST DESIGNATION	SHEAR STRENGTH **MPa (psi)**	SHEAR STRAIN		SHEAR MODULUS **GPa (Msi)**
		Elastic	Maximum	
C-75-11L	13.9±1.4 (2013.4±201.4)	0.0035	0.0039	3.56 (0.575)
C-100-11L	15.5±1.2 (2243.8±171.2)	0.0029	0.0037	5.35 (0.774)
C-150-11L	15.0±1.1 (2176.8±165.8)	0.0026	0.0038	5.77 (0.837)
C-XR-11L	13.4±0.9 (1946.8±132.3)	0.0030	0.0035	4.47 (0.649)
C-75-16L	14.7±7.2	0.0035	0.0038	4.20 (0.609)
C-100-16L	(2132.2±1038.9)	0.0052	0.0056	3.17 (0.460)
C-150-16L	16.5±3.0 (2390.8±437.4)	0.0048	0.0051	4.42 (0.640)
C-XR-16L	21.2±3.2 (3070.3±456.2)	0.0034	0.0038	5.00 (0.724)
	17.0±0.8 (2462.4±122.3)			

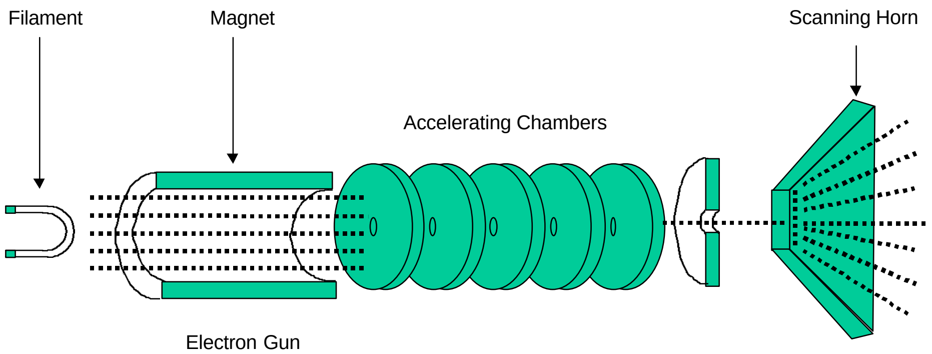

Figure 1: Schematics of a Typical Accelerator

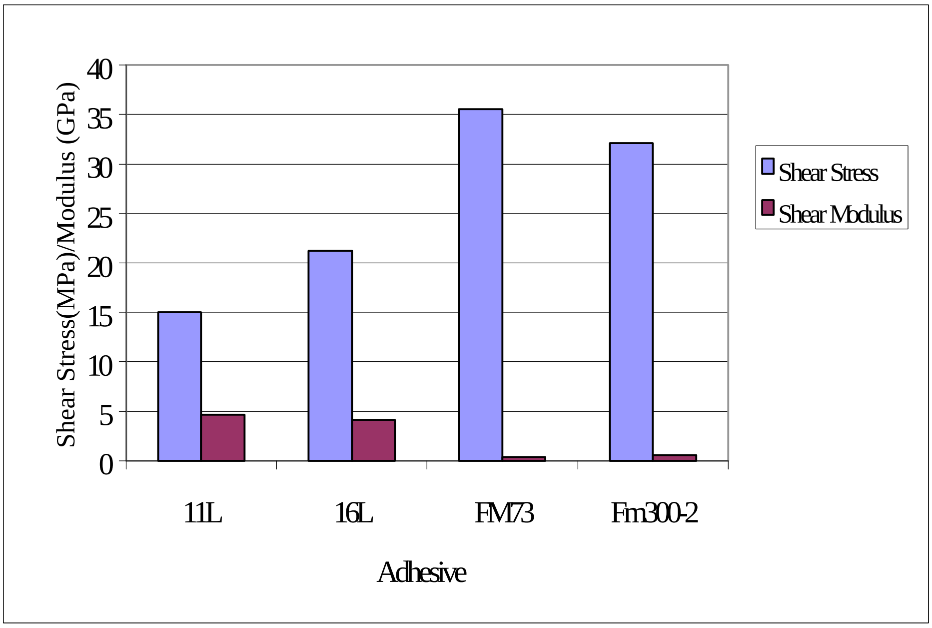

Fig. 1: Single lap shear strengths of EB/X-ray adhesives

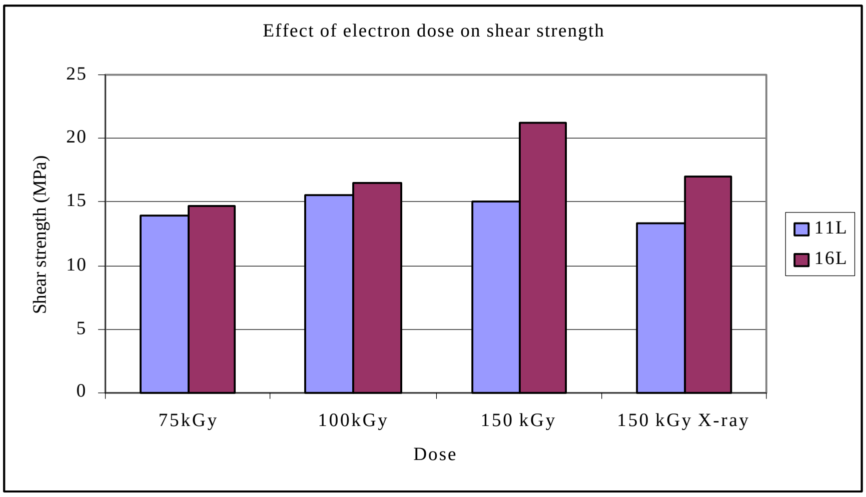

Figure 2: Effect of electron dose on shear strength properties of electron beam adhesives

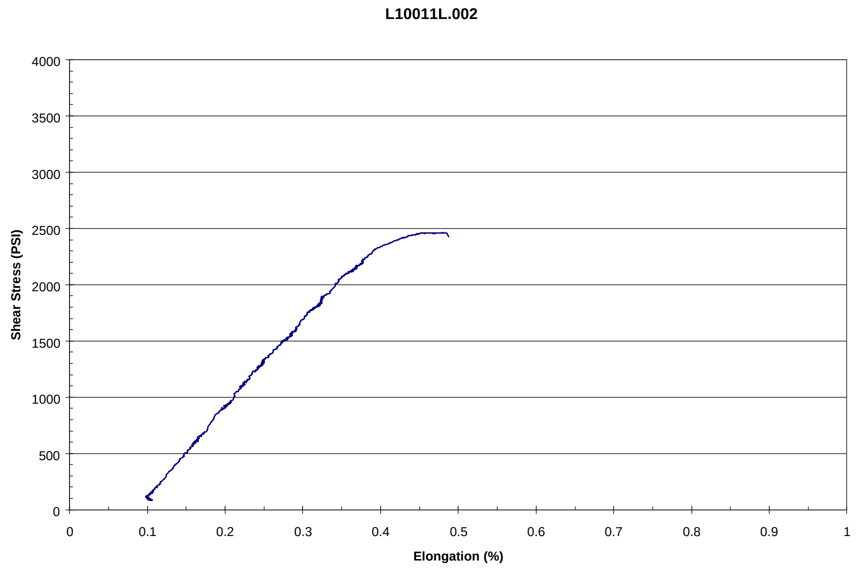

Figure 3: Typical shear stress-shear strain curve for 11L

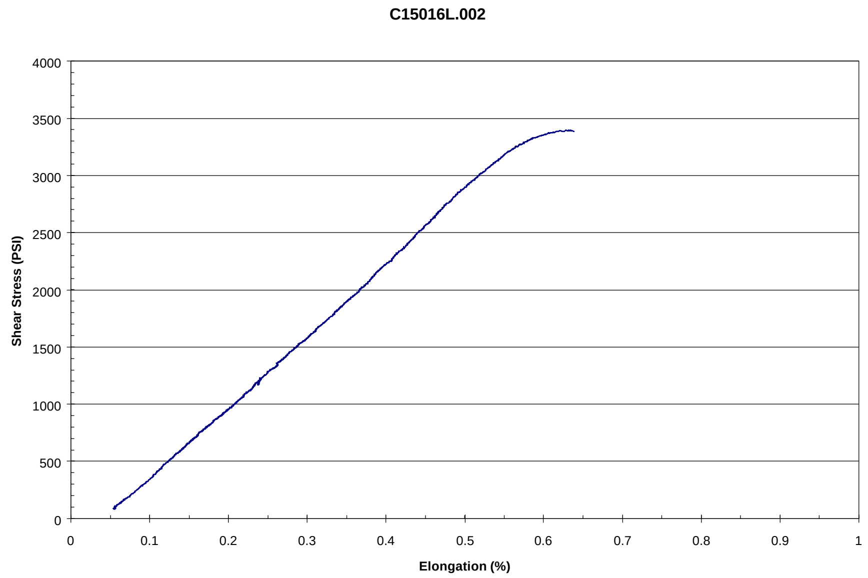

Figure 4: Typical shear stress-shear strain curve for 16L