



# Environmental Issues for Polymer Matrix Composites and Structural Adhesives

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ARL-RP-27

June 2001

A reprint from *Clean Products and Processes*, vol. 2, pp. 228–235, 2001.

20010801 052

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## Abstract

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The U.S. Department of Defense (DoD) has been utilizing polymer matrix composite (PMC) and structural adhesive materials in military equipment for over 20 years. However, the volume of PMCs in fielded systems has remained relatively low. Currently, however, the DoD has established strategic goals that will necessitate the use of lightweight composites in order to meet performance requirements. Therefore, the volume of composites used in DoD systems is expected to see an unprecedented 100-fold increase over the next 30 years. As production volumes increase, the need to address environmental impact increases. The major contributions to environmental degradation from composites are generation of hazardous air pollutants (HAPs) and generation of hazardous (HW) and solid wastes. HAPs result primarily during the curing of the composite. HWs arise from expiration of stockpiled resin materials and from soiled support media used during manufacturing and clean up. Due to the wide range of applications and materials systems, as well as manufacturing and repair requirements, a family of environmentally benign solutions is needed to reduce and eliminate environmental impacts from PMC manufacturing. Solutions are proposed involving use of new technologies and materials to reduce pollutants from composite manufacturing. The technologies proposed include alternative curing of thermoset composites using electron beam (E-beam) irradiation and materials substitution employing thermoplastics processed using electromagnetic irradiation.

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228

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**Keywords** Polymer matrix composites · Pollution · Electron beam · Induction

## Introduction and overview

Polymer matrix composites (PMCs) are strong candidates for many load-bearing structures in both commercial and

military applications. The high strength-to-weight and stiffness-to-weight ratios of PMCs make them attractive solutions for high performance structures where weight reductions can enable enhanced performance. PMCs are gaining visibility as the traditional high costs associated with these materials are reduced and consumer applications are more commonplace. For example, the use of PMCs – particularly carbon fiber reinforced composites – in sporting goods and recreational products has exploded in recent years and the public has an increased awareness of these unique materials. Transportation applications of PMCs including automotive and aerospace usage have also risen dramatically over the last decade. Continued and increased use of composites in military applications can be expected over the next several years as all services have requirements to increase mobility and deployability of their forces. However, the impact of the current composite materials and processing techniques on the environment is of increasing concern as the manufactured volume of PMCs rises. Research at our laboratories has focused on providing potential solutions to the environmental impact of composites manufacturing and repairs.

The U.S. Department of Defense (DoD) anticipates a 100-fold increase in the use of composites over the next 30 years. Currently, PMCs are used in fielded military applications that include helicopter rotorblades, Naval surface ship superstructures, high-performance aircraft, and multi-service munitions. These military systems have demonstrated that PMCs have superior performance and reduced parasitic weights. Consequently, new military systems are being developed that take advantage of PMC material characteristics, which will result in a significant increase in DoD production of PMCs. The use of PMC materials will result in a lighter military force, with increased combat performance, increased combat range, and reduced logistical support requirements. Among the scheduled DoD programs that will utilize PMCs are the Army's Future Combat Systems (FCS), naval DD21 surface ship superstructures, and the Joint Strike Fighter (JSF). Conservative estimates propose that PMC usage will increase by two orders of magnitude by 2028. In addition, the use of structural adhesives will increase by a factor of twenty as high-strength high-durability adhesives (Fink et al. 1999) replace mechanical fasteners.

To understand the potential environmental impact of PMCs, it is important to consider the composition of constituents, byproduct formation, and the processing/manufacturing methods that are used to form PMC struc-

Received: 25 April 2000 / Accepted: 25 July 2000

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tures. PMCs are commonly composed of rigid reinforcements (e.g., fibers, fillers, etc.) embedded in a polymer matrix. The polymer can range from low molecular weight monomers (oligomers) used in thermosetting materials to pre-reacted high molecular weight polymers for thermoplastic applications. Consequently, composite processing is dependent upon the polymer matrix. The broad range of polymer properties gives rise to the various forms of composite materials, including prepreg (neat-resin-impregnated fabrics to form a tacky solid fabric), neat-resins (that can infuse a fiber-fabric during molding), and filled resins (Seferis and Nicolais 1983). A partial list of industrially used resins, reinforcements, and processing methods for composites is shown in Table 1.

Composite materials, despite their broad application, are not environmentally benign. Among the environmental concerns in PMC manufacture are generation of hazardous air pollutants (HAPs) and hazardous wastes (HWs). HAPs associated with composite production include certain volatile organic compounds (VOCs), out-gassing of nitrous oxides (NO<sub>x</sub>), and emission of hazardous constituents. Organic solvents are used in composite manufacturing as processing and cleaning aids and, if not properly handled, are released as VOCs into the environment.

Once processed (cured), the composite materials are relatively inert. However, since composite materials are often processed directly from starting materials that may be hazardous, there is a potential for these species to be introduced into the environment as HW. The HWs associated with composites are generally found in uncured resins and are disposed of without being processed for several reasons. First, expiration of stockpiled resin materials necessitates the disposal of the aged stock as HW. Second, composites manufacturing generally results in several byproducts that may be contaminated with hazardous ingredients. These include uncured scrap materials, soiled support media used during manufacturing, and clean-up wastes. As PMC usage increases,

emissions from composite processing operations present challenges to composite manufacturers and DoD repair depots to meet federal and state regulations on hazardous emissions.

The shelf-life expiration issue is very relevant for prepreg and adhesive-bonding scenarios and can be addressed to reduce potential PMC related environmental impact. Stored PMCs are subject to slow curing processes that result in a limited lifetime for raw material storage and handling. The shelf-life issue may become increasingly problematic within DoD where materials are maintained for repair. Current industrial practice requires a "just-in-time" (JIT) approach to the acquisition of these materials and uses cold storage to increase the shelf life of these materials. For military applications, readiness requirements and remote operating locations necessitate materials stockpiles and JIT may not be a suitable solution to the shelf-life problem.

Consequently, new technology is desirable for DoD PMC manufacturers to meet environmental challenges associated with PMCs as their use increases. The responsibility for developing new composites processing technology resides within the PMC manufacturing and user communities in order to reduce hazardous emissions and HW contributions substantially *before* production of new systems makes environmental compliance more difficult to obtain. Research has been initiated that addresses the environmental impact of composite materials and provides appropriate solutions that minimize the problem.

#### Environmental discussion

Hazardous air pollutants (HAPs) from certain volatile organic compounds (VOCs) and autoclave generated nitrogen oxides (NO<sub>x</sub>) are released during manufacturing and repair of PMCs. In addition, hazardous and solid wastes are produced by PMC processing because many of the starting components of the composite are classified by the U.S. Environmental Protection Agency (EPA) as hazardous constituents, as outlined in Title 40 of the Code of Federal Regulations (40 CFR.261). HWs originate from disposal of expired materials and contaminated scrap materials.

#### Hazardous emissions produced during cure

Composite materials and adhesives are generally processed using heat and pressure to fabricate the final article. Volatile organic compounds (VOCs) are released from the resins during processing. Certain VOCs react photochemically in the atmosphere to form tropospheric ozone, and their emissions are regulated. Typical VOC contents evolving from composites during processing range from 2% by weight for epoxy systems to 15% by weight for polyimides (Fink et al. 1999). Federal and state regulations on VOC emissions have already impacted production of composites in certain areas of the country (Fink et al. 1999). The standard processing methods for reducing VOC emissions are closed processing and accelerated curing of materials to react or trap VOCs within the curing media.

Table 1. Composites resins, reinforcements, and process technologies in current manufacture

Resins	Reinforcements	Product forms/ processing techniques
Imides	Carbon fiber	Prepreg
Polyesters	S2-glass fiber and fabric	Hand-lay-up
Vinyl esters	E-glass fiber and fabric	Vacuum Assisted Resin Infusion
Urethane	Woven polymer, e.g., polyimide, polyethylene, polyester, polyurethane	Resin Transfer Molding (RTM)
Epoxy, epoxy-amine, epoxy-anhydride, epoxy-amide	Non-woven polymer	
Phenolic		
Polyetherimide		

Nitrogen or nitrous oxides (NO<sub>x</sub>) emissions include nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), and nitrogen tetraoxide (N<sub>2</sub>O<sub>4</sub>), which are emitted from combustion sources, such as ovens and autoclaves. These gases affect ozone and are regulated as hazardous emissions. The greatest source of NO<sub>x</sub> in composites manufacturing and repair is autoclave curing. A select sample of composite materials for aerospace applications was used to determine typical emissions from a standard autoclave cure cycle. Autoclave NO<sub>x</sub> emissions were measured at 0.02 kg (or 2/3 mol) NO<sub>x</sub> per kilogram of composite (Fink et al.1999). For adhesives, NO<sub>x</sub> emissions are higher, approaching 0.2 kg (2 2/3 mol) NO<sub>x</sub> per kilogram. The adhesive emissions tend toward higher weight ratios

because the volume of adhesive to the volume-bonded materials (e.g., composite or aluminum panels) is small.

#### Hazardous constituents in PMCs and adhesives

The hazardous constituents most frequently found in PMCs are low molecular weight and aromatic hydrocarbons, amine curing agents, and various catalysts. Some of these materials have carcinogenic or mutagenic properties (Fink et al. 1999). Table 2 lists some common raw materials used in composite resin formulations and the associated health risks. The presence of any of these controlled wastes makes the entire raw material a controlled hazardous substance. Therefore, the elimination or reduction of hazardous constituents by substi-

Table 2. Carcinogenic and mutagenic health risks from composite resin constituents

	Chemical name	Carcinogen	Mutagen
Epoxy	Bisphenol A	No data available	Potential mutagen
	Diglycidyl ether of bisphenol A, C <sub>21</sub> H <sub>24</sub> O <sub>4</sub>	IARC Group 3 unclassified carcinogen to humans	Ames test both positive and negative results
	Epichlorohydrin, C <sub>3</sub> H <sub>5</sub> ClO	IARC Group 2A probable carcinogen to humans	Mutagenic activity in bacteria, animal tests positive
Epoxy curing agents	Tetraglycidylbis ( <i>P</i> -amino-phynyl) methane	IARC Group 3 unclassified carcinogen to humans	Ames test positive
	Boron trifluoride, BF <sub>3</sub>	IARC Group 3 unclassified carcinogen to humans	No data available
	4,4'-Methylene bis (2-cholor-aniline) (MOCA), C <sub>13</sub> H <sub>10</sub> Cl <sub>2</sub> O <sub>2</sub>	IARC Group 2A probable carcinogen to humans	Ames test positive
	4,4'-Methylenedianiline (MDA), C <sub>13</sub> H <sub>14</sub> N <sub>2</sub>	IARC Group 2B possible carcinogen to humans	No data available
	Diethylenetriamine (DETA) C <sub>4</sub> H <sub>13</sub> N <sub>3</sub>	No data available	Positive results in cultured mammalian cells
	Triethylenetetramine (TETA), C <sub>6</sub> H <sub>18</sub> N <sub>4</sub>	Not classified	Ames test positive, found to be a direct acting mutagen
	Dicydiamide (DICY), C <sub>2</sub> H <sub>4</sub> N <sub>4</sub>	Has not been investigated	Has not been investigated
Vinyl ester	4,4'-Sulfodianiline (DDS), C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	Similar to MDA	Similar to MDA
	Styrene, C <sub>8</sub> H <sub>8</sub>	IARC Group 2B possible carcinogen to humans	Positive in vivo tests of animals
Vinyl ester curing agents	Divinylbenzene, C <sub>10</sub> H <sub>10</sub>	no data available	No data available
	Benzoyl peroxide, C <sub>14</sub> H <sub>10</sub> O <sub>4</sub>	IARC Group 3 unclassified carcinogen to humans	No data available
	Methyl ethyl ketone peroxide, C <sub>8</sub> H <sub>16</sub> O <sub>4</sub>	No data available	No data available
	2,5-Dimethyl-2,5-di(2-ethyl-hexanoyl peroxy)hexane, C <sub>24</sub> H <sub>46</sub> O <sub>6</sub>	No data available	No data available
Phenolic	Cumene hydroperoxide, C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	No data available	Ames test positive
	Phenol, C <sub>6</sub> H <sub>6</sub> O	IARC Group 3 unclassified carcinogen to humans	no data available
Phenolic curing agents	Formaldehyde, CH <sub>2</sub> O	IARC Group 2A probable carcinogen to humans	Positive in bacterial tests and in isolated human and animal tests
	<i>p</i> -Phenolsulfonic acid, sodium salt, C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> Na	Byproduct sulfuric acid mist is a Group 1 carcinogen	No data available
	<i>p</i> -Toluenesulfonic acid, C <sub>7</sub> H <sub>8</sub> O <sub>3</sub> S × H <sub>2</sub> O	Byproduct sulfuric acid mist is a Group 1 carcinogen	No data available
Urethane	Methylenedi- <i>p</i> -Phenyl Diisocyanate (MDI), C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>	IARC Group 3 unclassified carcinogen to humans	No data available
Urethane curing agents	Toluene-2,6-diisocyanate, (TDI) C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	IARC Group 2B possible carcinogen to humans	Positive in a number of vitro tests
	4,4'-Methylene bis (2-cholor-aniline) (MOCA), C <sub>13</sub> H <sub>10</sub> Cl <sub>2</sub> O <sub>2</sub>	IARC Group 2A probable carcinogen to humans	Ames test positive

tuting or replacing some or all of these constituents can improve the environmental handling and safety of composite manufacturing operations.

When compared with traditional structural materials (metals, wood, etc.), composites are unusual in that many of the available product forms are supplied as raw materials that are chemically processed and machined by the end-user to produce the final product. While this fabrication method imparts significant flexibility to composites manufacturing operations, the chemical processing and storage of raw materials produces waste and scrap. Uncured scrap material is handled as HW due to the hazardous contents in the raw material formulation. Another limitation of these resins is a limited shelf life. Expired material is uncured resin that has been stored beyond a guaranteed useful lifetime. Even though the chemical changes in the raw materials are small (<10% change), the resulting changes in processing properties (e.g., resin viscosity, tack, cure behavior) will produce composites with substandard mechanical properties. Therefore, materials processed after their expiration date cannot be guaranteed to meet performance requirements and design allowables. Generally, expired composite and adhesive materials are disposed of rather than processed and must be considered HWs due to their composition.

The shelf life of the PMC resins arises from slow, uncontrolled, curing reactions that occur during storage, transport, or handling of the raw materials. Traditional thermosetting composite resins are cured thermally, and the kinetics of the cure is strongly dependent on time and temperature. Because these reactions continually occur, a shelf life is usually defined by the resin manufacturer to ensure that properly stored raw materials will perform within performance specifications. The advancement of the curing resin towards its shelf life results from an associated chemical change in the resin. At the shelf life, these chemical changes correspond to an "expiration limit," which is a measurable chemical quantity using spectroscopy or other chemical detection methods. The time at which the chemical changes equal this expiration limit is defined as the experimental shelf life.

Figure 1 schematically illustrates the chemical changes that occur in four different resin systems of varying reactivity under equivalent storage. The dashed line represents the chemical changes (cure) associated with the expiration limit for these materials. The time at which each material crosses this expiration limit defines its shelf life. In this case, material A has the shortest shelf life since its chemical change during storage is more rapid than those of the other systems and reaches the expiration limit well before systems B–D. Conversely, material D never crosses the expiration limit and can be considered to have infinite shelf life. The other two systems represent materials that have intermediate shelf lives. The shape of each curve is defined by the chemistry of the system and can be controlled to produce materials with varied shelf lives.

Resins can be designed that minimize these slow reactions and significantly increase the shelf life beyond what is now available. Ideally, infinite shelf life can be achieved by pre-reacting the monomers to form a polymer prior to

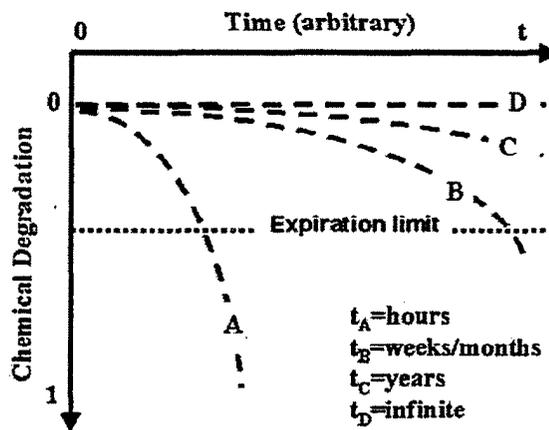


Fig. 1. Illustration of rate-dependent degradation of composite raw materials and adhesives. Shelf life is a defined time until performance losses are significant and is equated to a degree of raw material chemical degradation as an expiration limit. Materials that exceed the expiration limit are disposed as HWs by composite manufactures

storage. Thermoplastic polymer materials are an example of these materials that are not subject to chemical reactions during processing. However, thermoplastic polymers are not be easily adaptable for most composite applications, and therefore other chemical stabilizing methods must be employed to extend the shelf life of thermosetting materials.

The mass of processed HW from these composite operations will rise comparatively as new platforms are identified and improved with PMC structure as a component of their designs. Table 3 shows specified shelf life and out-time for a few widely used resins and prepregs. Table 4 shows similar characteristics for common structural adhesives. From the tables, typical shelf life for low- or room-temperature storage conditions is less than 1 year. Although these times provide conservative estimates of the performance limit of the raw materials, the expiration is often selected to limit liability of the material provider and has little connection to performance of the material. End-users are potentially discarding as HWs raw materials that may give acceptable performance, but the risk is unacceptable. This scenario contributes significantly to the HWs from PMC and adhesives use. Shelf life extension of the raw materials could provide savings both to the environment through hazardous and non-hazardous waste reductions and to composite manufacturing facilities by assuring quality materials for years rather than months.

We conducted a survey analysis of high-performance adhesive materials to determine approximate cure rates for room temperature storage. Each resin is a commercially available and autoclave curable adhesive or prepreg. The expiration specified for these materials by the manufacturers was 6 months at 0 °F. However, since we are interested in extending the ambient condition storage life of resins by eliminating the requirement for cold-storage, we evaluated the chemical degradation of these materials at room temperature. We defined the

**Table 3.** Resin stability under controlled low-temperature storage

Resin/fiber system	Processing temperature (°C)	Service temperature (°C, dry)	Shelf life at 18 °C (months)	Out-time at room temperature (days)
Epoxy/carbon fiber	120–180	80–230	6–12	10–30
Epoxy/aramid fiber	120–140	120	6	10–30
Epoxy/S-2 glass fiber	120–180	120–180	6	12
Bismaleimide/carbon fiber	180–250	230–320	6	28
Cyanate ester/carbon fiber	120–230	230–250	12	30
Cyanate ester/quartz fiber	120–180	90–180	6	21
Polyimide/quartz fiber	290–340	320	6	10

232

**Table 4.** Adhesive and resin stability under controlled low-temperature storage

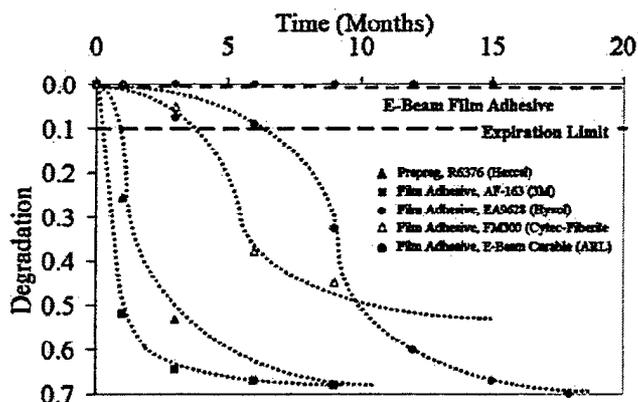
Resin or adhesive system	Processing temperature (°C)	Service temperature (°C, dry)	Shelf life at <4 °C (months)	Shelf life at <25 °C (months)	Out-time at room temperature
Derakane 411-C-50 epoxy vinyl ester	Room temperature	100	–	3 (dark, uncatalyzed)	10–60 min. (catalyzed)
Derakane 411-50 epoxy vinyl ester	Room temperature	100	–	6 (dark, uncatalyzed)	10–60 min. (catalyzed)
Derakane 470 epoxy vinyl ester	Room temperature	120–150	–	6 (dark, uncatalyzed)	10–60 min. (catalyzed)
Hysol EA 9390 2-part epoxy paste	90	180	12	6	2 h
Hysol EA 9394 2-part epoxy paste	Room temperature	180	12	12	1.5 h
Hysol EA 9396/C-2 2-part epoxy paste	90	200	12	12	8 h
Hysol EA 9695 epoxy film	120–180	150	6 at –19 °C	3	90 days
Redux 312 epoxy film	120	100	12	1	30 days
Redux 319 epoxy film	180	150	12	4	30 days
Redux 330 epoxy film	180	130	6	1.5	42 days

experimental expiration limit as a 10% nominal change in reactive chemical groups. Fig. 2 shows the resulting chemical degradation of the resins at room temperature as a function of time. All of the commercial systems degraded more than 10% within a few months. Even under cold storage conditions, all unused portions of these raw materials would be discarded as HWs within 6 months of purchase. The expired resins contain significant concentrations of controlled hazardous substances, which still pose an environmental hazard. The expired adhesive and composite resins are disposed as HW, creating unnecessary and expensive (U.S. \$ 55–110/kg) waste (Fink et al. 1999).

By way of contrast, newly developed composite raw materials that cure by electron beam irradiation showed no evidence of degradation at room temperature even after the year and a half of room temperature storage. The athermal cure initiation for the electron-beam-processed resins provides a significant chemical stability to these systems. Converting some composite applications from thermal processed adhesive and prepreg manufacturing techniques to alternative electron beam processing could increase storage life by more than a factor of four, substantially reducing HW contributions.

In addition to shelf-life expirations, process wastes also contribute significantly to the composites pollution problems. Process debris include scrap raw materials,

vacuum bagging materials, sealant, and shims. While the bagging, sealant, and shims are not hazardous materials, these often become contaminated with partially cured resins and adhesives during production and must be treated as HW. Conservative estimates suggest that production debris equivalent to one-third or one-half the



**Fig. 2.** Experimental determination of expiration for autoclave curable commercial adhesives and prepreps and experimental electron beam cured adhesives stored at room temperature. All the thermally curable materials expired rapidly at room temperature, while the electron beam adhesives showed no sign of aging after one and a half years of storage

equivalent mass of manufactured composite parts results (Fink et al. 1999).

### Potential solutions

No single source is responsible for the environmental impact of composite materials manufacturing. The issues are wide enough that many routes must be pursued to reduce the potential environmental impact. The broad range of materials, applications, and processing scenarios for composite repair and manufacture throughout DoD provide a host of target areas where the pollution contribution from composite manufacture can be reduced. In general, solutions can be pursued that reduce the VOC content of the starting materials, eliminate or reduce the NO<sub>x</sub> emissions associated with autoclave cure, or reduce the amount of hazardous ingredients introduced into the waste stream. Work has advanced in all three areas, but in this paper we report on specific routes that minimize the amount of hazardous constituents that are introduced into the environment from disposal of scrap and expired composite resins.

Two approaches can be pursued to eliminate or reduce the amount of material that is disposed. First, replacing thermoset resins that contain hazardous materials with thermoplastic polymers will completely eliminate hazardous constituents from the resin formulations. Furthermore, since thermoplastic resins are fully polymerized they have infinite shelf life. There are technical barriers associated with the implementation of thermoplastic resins that must be addressed to make them suitable for many composites applications. In instances where thermoplastic replacement of thermosets is not possible, technologies that extend the shelf life of PMC materials can minimize the flow of materials into the waste stream. In the following discussion, both approaches are discussed as potential solutions to these problems.

### Thermoplastic substitution of thermosets

An ideal way to eliminate hazardous constituents in composite processing is to develop methods to process raw materials that are environmentally benign. For example, substitution of heat-to-cure thermoset resins with heat-to-flow thermoplastics eliminates hazardous constituents from the waste scrap and provides essentially infinite shelf life. However, thermoplastic composites have not been widely accepted for PMC applications for a number of reasons. The largest hurdles preventing widespread use of thermoplastics in composite applications are processing limitations and performance limitations. The inherently high viscosity of thermoplastics introduces new processing challenges to the composites. High temperatures ( $T > 300\text{ }^{\circ}\text{C}$ ) are required to reduce a thermoplastic resin viscosity sufficiently to make high-quality composite components. In addition, the low thermal conductivity of thermoplastic materials makes achieving through-thickness heating difficult using traditional heating methods and lengthens the processing time. The elevated temperature processing requirement increases the cost and decrease the throughput of manufactured composites using thermoplastics. Therefore, new

heating and processing methods must be developed to meet the challenge.

One promising heating method that mitigates the heating issue is induction-based heating for rapid processing of thermoplastic composites. Induction heating provides volumetric heating of the composite, which enables very rapid processing to high quality composites. Induction heating of composite materials occurs through a number of complex interactions between a susceptor medium (graphite, carbon fibers, ferrites, etc.) and the bulk resin and has been recently reviewed (Wetzel et al. 1999). A large number of heat-generating mechanisms are responsible for the rapid heating and a thorough description is beyond the scope of this paper (Firko et al. 1998; Fink et al. 1996, 1998). However, the essential benefit of electromagnetic induction is *volumetric heating*, which eliminates many of the heat transfer limitations of traditional autoclave and hot-press processing methods. Because of the volumetric heating, induction processing enables rapid and cost effective processing of thermoplastic matrix composites, which may result in the replacement of thermoset composites with more environmentally benign thermoplastic matrices in the near future. Additional benefits of induction based thermoplastic composite processing include reduction of HAP emissions, particularly VOC and NO<sub>x</sub>, by eliminating the need for heated autoclaves.

Recent research on induction heating has advanced to the point where successful replacement of thermoset resins with thermoplastic composite processes has been accomplished. For example, in a large Army munition application, a thermoplastic prepreg material has been selected over a thermosetting material that had been used in earlier versions of the application. This simple substitution could eliminate hundreds of thousands of pounds of HW from the environment each year for a single application. Another example that also shows promise is the induction based fusion bonding of thermoplastic adhesives in place of thermosetting resins (Yarlagadda et al. 1998). Smart adhesive films that use ferromagnetic susceptors are now being developed which can be used to bond various substrates and eliminate the need for thermosetting materials that may contain hazardous ingredients. Additional research in induction processing will develop greater capabilities to allow replacement of hazardous thermosetting materials in more applications.

### Extended shelf-life thermosets

In many cases, thermosets are necessary to meet processing requirements in terms of viscosity and to provide performance. Additionally, thermoplastic adhesives have not been developed that are as effective as thermosetting counterparts. In this case, a solution to the environmental issues associated with waste from scrap and shelf life expiration is to produce materials with less hazardous constituents and extended (ideally infinite) shelf life. There are presently several research and development programs that provide materials with extended shelf life for use with current industrial practices (Fink et al. 1999; May et al. 1999). In a few cases these materials are available commercially, but they are not extensively used

because the substitutes do not meet the performance levels for structural applications. An approach to achieving extended shelf-life materials with equivalent performance to existing materials is the use of alternative curing technologies that are not thermally activated. By eliminating thermal curing mechanisms, raw materials aging can be minimized or eliminated. HWs that result from shelf-life expiration would be significantly reduced.

One non-thermal polymerization scheme includes the use of ionizing radiation, such as electron beam (E-beam), to initiate curing in the polymer matrix. E-beam curing is a process that uses high-energy electrons and/or X-rays to initiate polymerization and cross-linking reactions at controlled rates. Since the cure is not triggered until the resin is exposed to the E-beam irradiation, degradation reactions do not occur, resulting in exceptionally long shelf life for E-beam resins. Fig. 2 demonstrates the lack of chemical degradation occurring in E-beam resins over a 15-month period. However, the primary challenges facing the current SOTA E-beam resins are lack of toughness, low hot/wet operating temperatures, high costs of E-beam equipment, and radiation safety concerns (Janke et al. 1997a).

Many of the resin related shortfalls of E-beam materials have been addressed by introducing hybrid molecular structures including interpenetrating polymer networks (IPN). IPNs combine two or more networks that are cured independently. Successful E-beam formulated IPNs include both a step-growth epoxy-template and free-radical polymerized methacrylate (Goodman et al. 1996, 1997; Patrick et al. 1996). IPNs provide lower shrinkage and produce materials with wet operation temperatures approaching 150 °C, a performance that is more than adequate for some high-performance composite applications. Additionally, E-beam curable IPNs have been successfully toughened to meet structural performance requirements for DoD applications. In addition to IPN-type resins, radical cations are sometimes used to introduce radiation curing to thermosetting epoxies. Cationic induced curing occurs by adding an E-beam activated photoinitiator, such as diaryliodonium or triarylsulfonium salts (Janke et al. 1997b) to an epoxy matrix. The epoxy matrix homopolymerizes upon irradiation, which eliminates the need for hazardous amine curing agents (see Table 2). Elimination of the hazardous constituents and the potential for increased shelf life both provide significant environmental benefits compared with current composites processing technology. For instance, since E-beam composite processing occurs without firing an autoclave NO<sub>x</sub> production is eliminated. Further, the E-beam resins are processed at room temperature in the absence of any solvent media for the resin matrix, which reduces the VOC emissions associated with composite manufacturing.

### Summary

The use of PMCs continues to rise as industrial and military applications are identified where composites can improve performance and reduce costs. Currently, PMC manufacturers contribute only marginally to the HW generated within the U.S. DoD. However, as advanced

applications see increasing volumes of composites, the contribution from PMC manufacturing will rise. The pollutant impact of PMCs will increase proportionately with use unless environmentally friendly manufacturing alternatives are developed and implemented.

Hazardous air pollutants and HWs from PMC manufacturing can be reduced substantially by introducing non-autoclave-processing technology. Potential non-autoclave process techniques include substituting hazardous thermoset resins with high-temperature-processed thermoplastics. This approach eliminates pollution at the raw materials level. Additionally, increasing shelf life of materials by moving to E-beam cure of materials reduces the contribution of hazardous materials by increasing the storage potential for raw materials.

New and unique approaches to the pollution problem will continue to be necessary in order to stay ahead of the pollution problem and to preserve our environment for future generations.

### References

- Anonymous (1997) High performance composites. 1997 Sourcebook 27
- Fink BK, Gillespie JW Jr, McCullough RL (1996) Experimental verification of models for induction heating of continuous-carbon-fiber composites. *Polym Compos* 17:198-209
- Fink BK, McKnight SH, Gillespie JW Jr, Yarlagadda S (1998) Nano-particulate and conductive mesh susceptors for induction-based repair of composites. Proceedings of the 21st Army Science Conference: Science and Technology For Army After Next, Norfolk, Va., 15-17 June
- Fink BK, McKnight SH, Newton CH, Gillespie JW Jr, Palmese GR (1999) Non-polluting composites repair and remanufacturing for military applications: an environmental and cost-savings analysis. Army Research Laboratory Technical Report, ARL-TR-2139
- Firko J, Yarlagadda S, Gillespie JW Jr, Fink BK (1998) Optimization of heat generation in induction bonding using metal mesh susceptors. Proceedings of the ASC Thirteenth Technical Conference, American Society for Composites, pp 461-480
- Goodman DL, Palmese GR (1996) Composite curing with high energy electron beams: novel materials and processes. Proceedings of the 28th SAMPE Technical Conference, SAMPE, Covina
- Goodman DL, Byrne CA, Palmese GR (1997) Advanced electron beam curing and bonding of ground vehicles. Proceedings of the 43rd International SAMPE Symposium. SAMPE, Covina
- Janke CJ, Howell D, Norris RE, Gray J, Havens SJ (1997) Electron beam curing of polymer matrix composites. ORNL/M-6115, Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Janke CJ, Norris RE, Yarborough K, Havens SJ, Lopata VJ (1997) Critical parameters for electron beam curing of cationic epoxies and property comparison of electron beam cured cationic epoxies versus thermal cured resins and composites. Proceedings of the 42nd International SAMPE Symposium, SAMPE, Covina
- May CA, Wilson WA (1999) Ambient temperature storable thermoset prepreg resin system development for composite structures. ARL contractor report. Contract No. DAAL01-96-C-0111
- McKnight SH, Fink BK, Wells S, Yarlagadda S, Gillespie JW Jr (1998) Accelerated curing of epoxy paste adhesives for repair of composites using induction heating. Proceedings of ANTEC 98, Society of Plastics Engineers, Brookfield

- Patrick R, Palmese GR (1996) Radiation-induced free radical cure of resins for polymeric composites. Presented at the American Institute of Chemical Engineers Annual Meeting, Chicago, Ill., 13 November 1996
- Protection of the Environment. Title 40 Code of Federal Regulations P260 (1980) Amended 19 May 1980
- Protection of the Environment. Title 40 Code of Federal Regulations P261 (1980) Amended 19 May 1980
- Seferis JC, Nicolais L (eds) (1995) The role of the polymeric matrix in the processing and structural properties of composite materials. Plenum, New York
- Unser JF (1995) Advanced composites recycling/reuse program. Final report, WL-TR-95-7014, Wright Laboratory, Armament Directory, Eglin AFB, Fla., April 1995
- Wetzel E, Fink BK (1999) Feasibility of magnetic particle films for curie temperature-controlled processing of composite materials. Army Research Laboratory Technical Report. AR-TR-00
- Yarlagadda S, Gillespie JW Jr, Fink BK (1998) Resistive susceptor design for uniform heating during induction bonding of composites. *J Thermoplas Compos Mater* 11:321-337

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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project(0704-0188), Washington, DC 20503.

<b>1. AGENCY USE ONLY (Leave blank)</b>		<b>2. REPORT DATE</b> June 2001	<b>3. REPORT TYPE AND DATES COVERED</b> Reprint, January 1999–January 2000	
<b>4. TITLE AND SUBTITLE</b> Environmental Issues for Polymer Matrix Composites and Structural Adhesives			<b>5. FUNDING NUMBERS</b> 622618.H80	
<b>6. AUTHOR(S)</b> James M. Sands, Bruce K. Fink, Steven H. McKnight, Crystal H. Newton,* John W. Gillespie, Jr.,* and Giuseppe R. Palmese*				
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> U.S. Army Research Laboratory ATTN: AMSRL-WM-MB Aberdeen Proving Ground, MD 21005-5069			<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b> ARL-RP-27	
<b>9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)</b>			<b>10. SPONSORING/MONITORING AGENCY REPORT NUMBER</b>	
<b>11. SUPPLEMENTARY NOTES</b> A reprint from <i>Clean Products and Processes</i> , vol. 2, pp. 228–235, 2001. * Center for Composite Materials, University of Delaware, Newark DE 19716				
<b>12a. DISTRIBUTION/AVAILABILITY STATEMENT</b> Approved for public release; distribution is unlimited.			<b>12b. DISTRIBUTION CODE</b>	
<b>13. ABSTRACT (Maximum 200 words)</b> The U.S. Department of Defense (DoD) has been utilizing polymer matrix composite (PMC) and structural adhesive materials in military equipment for over 20 years. However, the volume of PMCs in fielded systems has remained relatively low. Currently, however, the DoD has established strategic goals that will necessitate the use of lightweight composites in order to meet performance requirements. Therefore, the volume of composites used in DoD systems is expected to see an unprecedented 100-fold increase over the next 30 years. As production volumes increase, the need to address environmental impact increases. The major contributions to environmental degradation from composites are generation of hazardous air pollutants (HAPs) and generation of hazardous (HW) and solid wastes. HAPs result primarily during the curing of the composite. HWs arise from expiration of stockpiled resin materials and from soiled support media used during manufacturing and clean up. Due to the wide range of applications and materials systems, as well as manufacturing and repair requirements, a family of environmentally benign solutions is needed to reduce and eliminate environmental impacts from PMC manufacturing. Solutions are proposed involving use of new technologies and materials to reduce pollutants from composite manufacturing. The technologies proposed include alternative curing of thermoset composites using electron beam (E-beam) irradiation and materials substitution employing thermoplastics processed using electromagnetic irradiation.				
<b>14. SUBJECT TERMS</b> polymer matrix composites, pollution, electron beam environment, induction, adhesive			<b>15. NUMBER OF PAGES</b> 23	
			<b>16. PRICE CODE</b>	
<b>17. SECURITY CLASSIFICATION OF REPORT</b> UNCLASSIFIED	<b>18. SECURITY CLASSIFICATION OF THIS PAGE</b> UNCLASSIFIED	<b>19. SECURITY CLASSIFICATION OF ABSTRACT</b> UNCLASSIFIED	<b>20. LIMITATION OF ABSTRACT</b> UL	

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