Health and safety in composites plants, Part I

By LaVerne Leonard, senior editor

Concern for worker safety has paired some strange bedfellows from industry, government, academia, and labor—and dissolved communications barriers, allowing a freer flow of health and safety information.

The widespread use of advanced composite materials brings with it a host of health-related challenges. This is largely because advanced composite technology evolved so rapidly that it outpaced the development of industrial hygiene procedures. But even more significant, perhaps, is the inherent chemical reactivity of aerospace-grade polymer matrix resins and their prepregs. When these materials are in an uncured or partially cured state, they present a variety of potential hazards to those who work with them. These hazards run the gamut from eye irritation and dermatitis to memory loss and cancer (Table I).

Although some of these potential hazards are formidable, advanced composites can be used safely in the workplace. This opinion is shared by health and safety professionals working in government, industry, and academia. The caveat is that proper industrial hygiene and engineering controls need to be in place, and workers must take certain precautions to protect themselves. These issues will be reviewed in the second part of this article, in the July/August issue of AC.

A rude awakening

Public awareness of the health aspects of advanced composites came via the media, in the summer of 1988. Stories about Boeing and Lockheed workers who allegedly were "poisoned" by the composite materials they handled were featured in newspapers and on national television. Interest in these stories was fueled by the fact that some of those afflicted were working in the “black world” (classified military aircraft programs) on the F-117A stealth fighter.

In the ensuing months, labor, industries, and various government agencies abandoned their adversarial roles and started working together. Their common goal was to avoid tough new regulatory pressures that could force segments of the U.S. aerospace industry abroad; they believed it could be achieved by ensuring good control of potential health effects. In order to hasten the process, they decided to organize a national forum to discuss the health aspects of advanced composites.

In February 1989, the first U.S. conference to address this subject was sponsored by the U.S. Air Force with the cooperation of the Suppliers of Advanced Composite Materials Assn. (SACMA) and the Aerospace Industries Assn. (AIA). At this gathering, a common commitment was made to an ongoing, proactive program to ensure the safety and health of aerospace workers.

A few weeks later, advanced composites were in the spotlight again, as a Senate subcommittee reviewed the use of the materials in the aerospace industry. Witnesses at the hearing included aerospace workers, a union spokesman, health and safety professionals, aerospace executives, and federal regulatory agents. (See "U.S. Composites Industry Health and Safety Concerns—A Brief History.")

At that congressional hearing, testimony given by various witnesses revealed some of the hazards associated with the use of aerospace-grade composites. George Robinson, director of occupational safety and health for the International Assn. of Machinists & Aerospace Workers (IAMAW), for example, told of the harmful effects of phenol formaldehyde resins and methylene diamine (MDA) curing agent.

Robinson referred to an epidemiological study done at the Boeing facility in Philadelphia on workers engaged in the fabrication of advanced composite components to be used in making helicopters. He said the study, conducted by the National Institute for Occupational Safety & Health (NIOSH), "detected an increased incidence of bladder cancer in workers exposed to MDA, the curing agent used in this advanced composite."

Another witness, Dale Daniels, executive vice president of Lockheed Aeronautical Systems Co. (Burbank, Calif.), also discussed the potential...
health problems associated with composites used in the aerospace industry. His testimony follows:

"Adverse health effects may occur following exposure to certain raw materials and processes. These potential adverse health effects are not unique to the aerospace industry. Composite-related exposures are most likely to occur through inhalation of dust, vapors, or fumes or when substances are absorbed through or react with the skin. Potential effects of the raw materials include skin, eye, and respiratory irritation and allergy, chronic lung disease, adverse reproductive effects, central-nervous-system depression, and damage to liver, kidneys, bone marrow, blood-forming systems, and lymphatic systems.

"Exposure to nonasbestos fibers can lead to scarring of the lungs. Some of these fibers have been found to cause cancer in laboratory animals. Two chemicals used as curing agents, methylene dianiline (MDA) and sulfonyl di-aniline, have been shown to cause cancer in laboratory animals (the danger to human beings is still unclear). MDA is a known liver toxicant, and some of the glycol ethers adversely affect reproduction. Heavy metals, including chromium VI (a carcinogen) and silver, are important constituents of pigments. Exposure to heavy metals may occur in a variety of ways that are unique to each pigment and process and may result in such varied health effects as cancer, gastrointestinal disorders, and damage to the nervous system.

"Additional health risks are posed if the raw materials are explosive or flammable. Improper mixing of epoxy resins from their component parts can create exotherms (forms of combustion) that may create heavy smoke. This smoke is filled with hazardous compounds. Workers can be burned if they come in contact with hot surfaces. When workers are cutting preimpregnated materials or are trimming, sanding, grinding, and drilling parts, they can be cut or they can suffer serious scrapes and bruises. These activities also create potential nuisance dust exposures."

Figure 2 is data Daniels presented at the hearing on worker compensation claims. AC recently spoke with Jim Ragsdale, Lockheed's director of communication. He reported that no Lockheed employee to date, through worker compensation claim, civil lawsuit, or other proceeding, has been determined...
to have been made ill as a result of working with composite materials.

In another part of Daniels' testimony, he said comments reported in the media in recent months had "cast an aura of mystery" over use of aerospace composites. He said it is important to note "the raw materials being used in aerospace—resins, catalysts, solvents, fabrics, fibers, inorganic ceramics, metal-containing pigments, and preimpregnated fabrics—are also in common use throughout U.S. industry."

**Chemicals to blame, not composites**

Members of SACMA believe that working with advanced composites is inherently "no more dangerous than working with conventional metals or a host of other potentially toxic chemicals in common use today." That was the message SACMA's executive director, Joseph Jackson, delivered to the American Conference of Governmental Industrial Hygienists in San Diego on March 5, 1991.

"This is neither to say that we know all there is to know about occupational health aspects of composite materials nor to dismiss worker concerns about real or perceived problems," Jackson said. "It is intended to say the

---

**U.S. composites industry health and safety concerns—a brief history**


June 2, 1988: Larry Werner of the Seattle Post-Intelligencer breaks story linking Boeing workers' illnesses with exposure to composites.


Fall 1988: Lockheed workers (about 100) in Burbank and Palmdale, Calif., file suits against their employer, claiming sickness associated to the use of advanced materials in the Stealth Bomber. Defendants in the Lockheed suits include Dupont for graphite/CFC solvents, GE for silicones, Ashland Chemical for MIBK and MIBK solvents, and other chemical companies.

December 1988: Boeing eliminates use of phenol and formaldehyde in a binding operation at its Auburn, Wash., plant.

Feb. 6-9, 1989: The U.S. Air Force sponsors a national conference on "Occupational Health Aspects of Advanced Composite Materials in the Aerospace Industry" in Dayton, Ohio. This conference, developed in cooperation with its Suppliers of Advanced Composite Materials and the Aerospace Industries Assn., draws more than 270 representatives from the Dept. of Defense and the service branches, industry, labor, and other federal agencies.

March 6, 1989: Congressional hearing on "Use of Toxic Materials in the Aerospace Industry" before the Senate Subcommittee on Toxic Substances, Environmental Oversight. Research, Development, is chaired by Sen. Harry Reid (D-Nev.). Witnesses include aerospace workers, union spokespeople, health/safety professionals, Boeing and Lockheed executives, and federal regulatory agencies.

February 1989: Lockheed is served 440 health and safety citations by OSHA, with fines totaling $1.6 million, for conditions in Building 199 and about 20 other smaller buildings in the Burbank plant.

April 13, 1989: SACMA and the AIA sign memorandum of understanding (MOU) in order to improve composite material labeling and facilitate circulation of safety data.

April 19, 1989: SACMA begins distributing its 30-page document "Safe Handling of Advanced Composite Material Components: Health Information." Booklet is intended to assist current and prospective users with proper handling of advanced composite products. It will supplement health and safety information published by the material suppliers.

May 1989: Boeing workers' injury claims denied.

April 18, 1990: Congressional Caucus on Advanced Materials hears SACMA's executive director Joe Jackson and International Assn. of Machinists & Aerospace Workers' occupational safety and health director George Robinson talk about protecting the aerospace worker. Caucus co-chair Sen. John McCain (R-Ariz.) pledges to support SACMA's recommendation to increase funding for federal initiatives that will improve health and safety for workers in advanced materials.

April 25, 1990: Epoxy Resins Workshop, cosponsored by the Society of the Plastics Industry and the U.S. Environmental Protection Agency, is held in Washington, D.C. Talks by both agency and industry address Section 5, Manufacture Notifications and Consent Orders, and Section 4, Test Rules, issues as they relate to glycidyl derivatives.

March 5-7, 1991: American Conference of Governmental Industrial Hygienists sponsors a conference on advanced composites in San Diego that attracts more than 100 health and safety specialists from across the United States as well as in Canada, Denmark, and Sweden.

causal agents are reactive chemicals, and the underlying problem is primarily a chemical-handling problem—not a specific composite materials problem."

In a recent interview, Jackson told AC that workers using advanced composites need to form new work habits. He said a big problem is convincing people who have worked with other materials that when they work with composites they are handling chemicals. "They should be attuned to that fact," Jackson says, "and they should pay careful attention to the Material Safety Data Sheets and to worker training programs."

Jackson also said that SACMA presently has a group of people working on neurotoxicity, starting their investigation with a general literature search. Meanwhile, he said, SACMA is hoping to loosen up some funds within the appropriate health agencies to conduct more research in this area. "I think we were seeing a lot of 'neuropid' effects in the Lockheed and Boeing situations several years ago," he said. "And those are mixed chemical reactions, or things that are just neurotoxins, which have a different kind of effect on people, obviously."

Reactive agents at work

There's no shortage of potentially hazardous materials in an aerospace plant. At Lockheed's operation in Burbank, for example, thousands of different chemicals are routinely used. Some of the most reactive of these, not surprisingly, are the raw materials used in aerospace composites—solvents, curing agents, and resins. In the event of careless handling, it is the reactivity of these products that can lead to impairment of health.

Resin systems used in aerospace applications are typically complex formulations of polymerizable molecules, catalysts, and solvents (see "Polymer Matrix Resin Systems"). The most commonly used matrix materials in the advanced composites industry today are the epoxy resins, which include some exceptionally chemically reactive epoxide groups.

The major health concerns currently associated with epoxides are cancer and reproductive toxicity. This information was presented at the Epoxy Resins Workshop by Flora Chow of the Environmental Protection Agency. The workshop, held in Washington, D.C., on April 25, 1990, was sponsored by the EPA and the Society of the Plastics Industry Inc.—two groups that more typically find themselves on opposite sides of the table.

Another speaker at the workshop was Shell Oil staff toxicologist Thomas Gardiner. He discussed the effects of inhalation exposure to members of the epoxide category called glycidyls, which "target the liver, lungs, and kidneys." Gardiner also noted that some data suggest that testicular atrophy may be a reproductive health concern for some lower-molecular-weight compounds, such as allyl glycidyl ether (AGE).

The reactivity of the epoxide groups is only part of the problem, however. Epoxy resins are always used with curing agents (hardeners) that are particularly complex:

- An epoxy formulation is principally a mixture of molecules containing one or more epoxide groups and a coreactant called the curing agent. The 1,2(epoxides are exceptionally chemically reactive, and will react with a broad class of chemical types, including acids, anhydrides, amines, alcohols, phenols, mercaptans, and water. Many epoxy systems can be partially cured by heat alone. Catalysts are necessary to cause all of the reactive groups to combine and participate in crosslinking during molding.
- The polyester resins used for advanced composites contain difunctional or trifunctional molecules in the molecular backbone to permit adduct-type, crosslinking reactions. The unsaturated polyester is obtained from the resin manufacturer as a low-molecular-weight (1000 to 4000) prepolymer, generally assembled from three or more monomeric materials. These are typically an aromatic acid for molecular rigidity, an acid or anhydride containing the double bond, and a glycol that corresponds loosely to the curing agent in epoxy-based chemistry.

also highly reactive materials. The aromatic amine hardeners, for example, have been shown to cause damage to internal organs, specifically the liver, and may decrease the ability of the blood to transport oxygen to the tissues.

Health concerns are also associated with the use of solvents and other matrix resins such as the phenol formaldehydes and isocyanates. Toluene diisocyanate (TDI), for example, is a highly toxic material that may cause respiratory sensitization. Once a person becomes sensitized, allergic reactions may be seen upon exposure to TDI at only a few hundredths of a part per million (see Table II).

Detailed information on these materials, and other potentially hazardous components of advanced composites, is documented in SACMA's booklet entitled "Safe Handling of Advanced Composite Materials Components: Health Information." An expanded version, which is supposed to be 20 percent longer than the original, is scheduled to be released in June.

Save your skin
At the Navy Aviation Depot (NADEP) at North Island (San Diego), experience with composite materials points to one definite area of worker risk: contact dermatitis (Figure 3) resulting from exposure to epoxy resins. "There are two other areas of concern," adds Capt. Edward Doyle, "hepatitis due to the increasing use of MDA, and lung disease due to exposure to dust generated from..."
Contact dermatitis caused by materials such as epoxy resins usually is located on the workers' hands, arms, and faces. (Photo: Norman Levine, University of Arizona Medical Center, Div. of Dermatology, Tucson)

grinding the carbon/epoxy laminate.

Doyle, who is in Naval Environmental Preventive Medicine, shared this information with attendees at the March 1991 ACGIH Conference on Advanced Composites. He also says reactive airway-dysfunction syndrome (RADS), which could result from a significant inhalation exposure to a resin exotherm, and mass psychogenic illness syndrome are “possible, although unlikely in the NADEP setting.”

Doyle’s findings at NADEP, particularly the predominance of dermatitis, are typical of the experiences of other aerospace facilities. The Aerospace Industries Association’s (AIA) in-depth health and safety survey of member companies revealed a similar pattern. Results indicated that the most prevalent potential hazards associated with working with advanced composites are skin and eye irritation when personnel are exposed to resin, resin vapors, and fiber matrices.

“When you’re dealing with chemically reactive resins, vapors, and fibers, there is one guiding principle that holds true,” says Melvin Kantz, formerly director of research and development for Ferro Corp. Composites Div. (Los Angeles). “Without exposure, there can be no hazard.” Thus, he says, every reasonable precaution should be taken to prevent contact of these materials with the body.

In a fabrication shop, this means that workers must never touch resins and prepregs with unprotected hands; they must never allow gloves and contaminated clothing to touch their faces, eyes, and other exposed skin; and they must not breathe volatile matter and dust given off by or from these materials. “A worker should no more readily contact an uncured matrix resin or prepreg than he or she would put an unprotected hand in a chromate plating bath or operate a stamping press or welding torch without suitable protection,” Krantz says.

He explains that dermatitis may be mild, involving only redness and itching—or quite severe, when the allergic reaction takes the form of asthma in particularly sensitive individuals. “Once an individual is sensitized, only minimal...
When anyone reacts with some allergy to the following may happen. The most common in the order of reaction:

1. Skin irritation
2. Asthma
3. Allergic rhinitis
4. Eye irritation
5. Erythematosus rash
6. Lifethreatening reaction

Another possible reaction may include: shortness of breath, hives, rash, urticaria, a high fever, changes in the mouth, and swelling of the throat. In this case, the victim should be taken to the hospital immediately. The victim should have had a previous reaction to a similar substance, or he or she should have been sensitized to it earlier in the day.

Allergic reactions are a constant threat to the safety of composite workers. Since they are such a prevalent problem, SACMA decided to combat the problem via education. The result of its efforts is a training video and handbook entitled “Save Your Skin!” (Figure 4). The video takes a mildly humorous approach to the problem, but does a good job of covering the basics. Used in combination, the materials should heighten worker awareness about dermatitis and provide general guidelines that will complement the employer’s chemical-handling procedures.

Note: Part II of this article will discuss measures that can be taken to reduce the risks associated with handling advanced composites from personal protective equipment to engineering controls.

References


Rheology helps you to optimize your Process, your Material, and your Quality. Finding the viscosity minimum, as we did with this 31858 Phenolic compound, is only the beginning.

So come and work with the professionals.

1-800-688-FLOW (3569)

Your Rheology Hotline.

For more information on purchasing materials from SACMA, circle the appropriate numbers on the Reader Service Card.

Safe Handling of Advanced Composite Materials Components: Health information 204
Save Your Skin 205