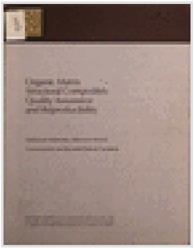


Organic Matrix Structural Composites: Quality Assurance and Reproducibility (1981)

National Materials Advisory Board; Commission on Sociotechnical Systems; National Research Council

Pages
159

Size
8.5 x 10

ISBN
0309331188

TN 690 .074 1981

Organic matrix structural
composites

NATIONAL RESEARCH COUNCIL
ISSION ON SOCIOTECHNICAL SYSTEMS

NATIONAL MATERIALS ADVISORY BOARD

Chairman

Mr. William D. Manly
Senior Vice President
Cabot Corporation
125 High Street
Boston, MA 02110

PAST CHAIRMAN

Mr. Julius J. Harwood
Director, Materials Science Lab
Engineering and Research Staff
Ford Motor Company
P.O. Box 2053
Dearborn, MI 48121

Members

Dr. H. Kent Bowen
Professor, Ceramic and
Electrical Engineering
Massachusetts Institute
of Technology
77 Massachusetts Avenue
Cambridge, MA 02139

Dr. William J. Burlant
Manager, Materials Technology
Operations
General Electric Company
Engineered Materials Group
500 W. Wilson Bridge Road
Columbus, OH 43285

Dr. George E. Dieter, Jr.
Dean, College of Engineering
University of Maryland
College Park, MD 20742

Dr. Larry L. Hench
Professor and Head
Ceramics Division
Department of Materials
Science & Engineering
University of Florida
Gainesville, FL 32601

Dr. Nick Holonyak, Jr.
Professor Electronic Engineering
University of Illinois-Urbana
Department of Electrical Engineering
Urbana, IL 61801

Dr. John R. Hutchins III
Senior Vice President and Director
Research and Development Division
Corning Glass Works
Sullivan Park
Corning, NY 14830

Dr. Sheldon E. Isakoff
Director, Engineering Research
and Development Division
E. I. du Pont de Nemours
& Company, Inc.
Wilmington, DE 19898

Dr. Frank E. Jaumot, Jr.
Director of Advanced
Engineering
Delco Electronics Division
General Motors Corporation
P.O. Box 1104
Kokomo, IN 46901

Dr. Alan Lawley
Professor Metallurgical Engineering
& Chairman, Materials Engineering
Department
Drexel University
Department of Materials Engineering
Philadelphia, PA 19104

Dr. James W. Mar
Professor, Aeronautics and
Astronautics, Bldg. 33-307
Massachusetts Institute
of Technology
Cambridge, MA 02139

Dr. Raymond F. Mikesell
W. E. Miner Professor of Economics
University of Oregon
Department of Economics
Eugene, OR 97403

Dr. R. Byron Pipes
Director, Center for
Composite Materials
Department of Mechanical &
Aerospace Engineering
University of Delaware
Newark, DE 19711

Dr. Brian M. Rushton
Vice President, Technology
Celanese
1211 Avenue of the Americas
New York, NY 10036

Dr. Allen S. Russell
Vice President, Science
& Technology
Aluminum Company of
America
1501 Alcoa Building
Pittsburgh, PA 15219

Dr. John J. Schanz, Jr.
Senior Specialist
Congressional Research
Service-ENR
Library of Congress
Washington, DC 20540

Dr. Arnold J. Silverman
Professor
Department of Geology
University of Montana
Missoula, MT 59801

Dr. Dorothy M. Simon
Vice President & Director
of Research
AVCO Corporation
1275 King Street
Greenwich, CT 06830

Dr. Roger A. Strehlow
Professor, Aeronautical and
Astronautical Engineering
University of Illinois
Urbana
101 Transportation Building
Urbana, IL 61801

Dr. Michael Tenenbaum
1644 Cambridge
Flossmoor, IL 60422

Dr. William A. Vogely
Professor and Head
Department of Mineral Economics
Pennsylvania State University
University Park, PA 16802

Dr. Albert R. C. Westwood
Director, Martin Marietta Labs
Martin Marietta Corporation
1450 South Rolling Road
Baltimore, MD 21227

NMAB Staff

R. V. Hemm, Acting Executive Director

2-81

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER NMAB-365

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Organic Matrix Structural Composites:
Quality Assurance and Reproducibility

5. TYPE OF REPORT & PERIOD COVERED Final Report

6. PERFORMING ORG. REPORT NUMBER NMAB-365

7. AUTHOR(s)
Committee on Characterization of Organic Matrix Composites
National Materials Advisory Board

8. CONTRACT OR GRANT NUMBER(s) MDA-903-78-C-0038

9. PERFORMING ORGANIZATION NAME AND ADDRESS
National Materials Advisory Board
2101 Constitution Avenue, N.W.
Washington, D.C. 20418

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Department of Defense
National Aeronautics and Space Administration

12. REPORT DATE 1981

13. NUMBER OF PAGES 156

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report) Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

[redacted]

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)
Distribution limited to U.S. Government agencies only; T&E May, 1981. Other requests for this document must be referred to DARPA, 1400 Wilson Boulevard, Arlington, VA 2209.

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

advanced composites
organic matrix
reinforcing fibers
prepreg
characterization
fabrication
unidirectional ply
structural design
predictive life tests
accelerated testing
nondestructive evaluation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The use of organic matrix advanced composites as primary (system critical) structures has increased rapidly. As a consequence of this rapid growth there has not been the opportunity to develop either the broad experience or technology base to use these composites with the same degree of confidence as with metallic alloys.

The first objective of this study was to survey and assess the state

of the art of organic matrix structural composites technology. The second goal was to formulate a set of recommendations to:

1. Assure by prior specification that fabricated structures will meet performance requirements;
2. Predict lifetime behavior through analysis and accelerated test methods; and
3. Provide verification methods for both, thus assuring product specification, and early indication of failure.

ORGANIC MATRIX STRUCTURAL COMPOSITES: QUALITY ASSURANCE AND REPRODUCIBILITY

Report of

THE NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems

National Research Council

Publication NMAB-365

National Academy Press

Washington, D.C.

1981

NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competence and with regard for appropriate balance.

The report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

The National Research Council was established by the National Academy of Sciences in 1916 to associate the broad community of science and technology with the Academy's purposes of furthering knowledge and of advising the federal government. The Council operates in accordance with general policies determined by the Academy under the authority of its congressional charter of 1863, which established the Academy as a private, nonprofit, self-governing membership corporation. The Council has become the principal operating agency of both the National Academy of Sciences and the National Academy of Engineering in the conduct of their services to the government, the public, and the scientific and engineering communities. It is administered jointly by both Academies and the Institute of Medicine. The National Academy of Engineering and the Institute of Medicine were established in 1964 and 1970, respectively, under the charter of the National Academy of Sciences.

The Commission on Sociotechnical Systems is one of the major components of the National Research Council and has general responsibility for and cognizance over those program areas concerned with physical, technological, and industrial systems that are or may be deployed in the public or private sector to serve societal needs.

The National Materials Advisory Board is a unit of the Commission on Sociotechnical Systems of the National Research Council. Organized in 1951 as the Metallurgical Advisory Board, through a series of changes and expansion of scope, it became the National Materials Advisory Board in 1969. Its general purpose is the advancement of materials science and engineering in the national interest. It fulfills that purpose by providing advice and assistance to government agencies and private organizations on matters of materials science and technology affecting the national interest, by focusing attention on the materials aspects of national problems and opportunities, and by making appropriate recommendations for the solution of such problems and the exploitation of the opportunities.

This study by the National Materials Advisory Board was conducted under Contract No. MDA-903-78-C-0038 with the Department of Defense and the National Aeronautics and Space Administration.

Printed in the United States of America.

ABSTRACT

The use of organic matrix advanced composites as primary (system critical) structures has increased rapidly. As a consequence of this rapid growth there has not been the opportunity to develop either the broad experience or technology base to use these composites with the same degree of confidence as with metallic alloys.

The first objective of this study was to survey and assess the state of the art of organic matrix structural composites technology. The second goal was to formulate a set of recommendations to:

(1) Assure by prior specification that fabricated structures will meet performance requirements;

(2) Predict lifetime behavior through analysis and accelerated test methods; and

(3) Provide verification methods for both, thus assuring product specification, and early indication of failure.

PREFACE

Organic matrix composites offer the user materials that are stiffer and stronger than steel and aluminum on a unit weight basis. Other desirable features include fatigue and corrosion resistance, damage tolerance, design flexibility, and end item life-cycle cost reduction.

A partial list of Department of Defense (DoD) and National Aeronautics and Space Administration (NASA) programs using or possibly using organic matrix composites includes the primary and secondary structures on many military aircraft: AV8B, B-1, C-5A, F-4, F-14, F-15, F-16, F-18, F-111, V/STOL-A, Army helicopters; NASA's Explorer 49, Pioneer 10, and Space Shuttle; and the DC-10, L-1011, and B-737 commercial aircraft. Composites are in use or are being developed for such commercial products as golf clubs, fishing rods, tennis rackets, truck springs, and drive shafts.

Composite materials are frequently used in sophisticated hardware in which the structures are subjected to severe environments, such as in aerospace technology. The manufacturers and purchasers of components for critical applications must be confident that structures made from composite materials are reliably and reproducibly produced; the consequences of failure could be disastrous, costing lives and loss of expensive equipment. Therefore, DoD and NASA, under their contract with the National Academy of Sciences, requested that the National Materials Advisory Board undertake a study of techniques that could be employed to monitor chemical and physical properties of composites at various stages of manufacture. The stages range from the outset of composite buildup, through fabrication and curing, to the final engineered structure undergoing either accelerated laboratory testing or in-service evaluation.

The Committee on Characterization of Organic Matrix Composites was formed and held an initial meeting on July 25 and 26, 1978. It was determined at that time that the study would provide the sponsors with recommendations designed to

1. Assure by prior specification that fabricated structures will meet performance requirements;

2. Predict lifetime behavior through analysis and accelerated test methods; and

3. Provide verification methods for both, thus assuring product specification, and early indication of failure.

The committee realized early in its deliberations that reliability of the final engineered structure could be enhanced by new material development and improved fabrication techniques; however, the main emphasis of the study was on ensuring the reproducibility of state-of- the-art materials and structures derived from these. A more detailed study of improved materials and fabrication techniques could be the subject of another committee's efforts.

The chairman wishes to thank all committee members and liaison representatives for their roles in completing this task. Appreciation is also extended to the following for information supplied to the committee: Dr. Richard Hoffman, Hercules, Inc.; Mr. Ray Loszewski, AVCO; Dr. Dick Wilkins, General Dynamics; Dr. Joseph Augl, Naval Surface Weapons Laboratory; Dr. Francis Chang, General Dynamics; Dr. Sanford Sternstein, Rensselaer Polytechnic Institute; Dr. James Seferis, University of Washington; Mr. Robert C. Goran and Dr. Clarence Wolf, McDonnell Aircraft; Dr. Paul McMahon, Celanese Corp.; Dr. William Hufferd, University of Utah; Mr. Vere Thompson, The Boeing Commerical Aircraft Co.; Dr. Herbert F. Volk, Union Carbide Corp.; Dr. Lynn Penn, Textile Research Institute; Dr. Zvi Hashin, Tel Aviv University; and Dr. Tito T. Serafini, National Aeronautics and Space Administration.

Dr. George S. Ansell, Chairman

COMMITTEE ON CHARACTERIZATION OF ORGANIC MATRIX COMPOSITES

GEORGE S. ANSELL, Rensselaer Polytechnic Institute, Troy, New York
Chairman

DONALD F. ADAMS, University of Wyoming, Laramie

JAMES E. CAREY, Plastics Industry Consultant, Mullica Hill, New Jersey

JAMES F. CARPENTER, McDonnell Aircraft, St. Louis, Missouri

ISAAC M. DANIEL, IIT Research Institute, Chicago, Illinois

FRANK P. GERSTLE, Sandia Laboratories, Albuquerque, New Mexico

JOHN K. GILLHAM, Princeton University, Princeton, New Jersey

R. BYRON PIPES, University of Delaware, Newark

FRANK P. SOLIMAN, Ewald Associates Inc., Detroit, Michigan

Liaison Representatives

CHARLES F. BERSCH, Naval Air Systems Command, Department of the Navy, Washington, D.C.

CHARLES E. BROWNING, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio

JOHN HURT, U.S. Army Research Office, Research Triangle Park, North Carolina

GEORGE R. THOMAS, Army Materials and Mechanics Research Center, Watertown, Massachusetts

NORMAN J. JOHNSTON, Langley Research Center, National Aeronautics and Space Administration, Hampton, Virginia

RICHARD LAUVER, Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio

NORBERT BIKALES, National Science Foundation, Washington, D.C.

NMAB Staff

STANLEY M. BARKIN, Staff Scientist

CONTENTS

SUMMARY

The brief summary presented here is a compilation of the major conclusions and recommendations in the report. For more details the reader is referred to the respective chapters of the report.

The committee believes that if the recommendations are followed, components for critical applications can be made more reproducibly from organic matrix composites.

Starting Components

Conclusions

1. Characterization and quality control of raw materials used to formulate the matrix resins are evolving. Physicochemical methods available to improve prepreg controls are being implemented.

2. Fiber characterization and control and the fiber-to-resin interface have received minimal attention compared with the recent efforts and resulting progress in the characterization of the matrix resin.

Recommendations

1. The purity required for each of the starting raw materials should be determined, and quality controls for composite-grade raw materials established. The minor impurities and the types and amounts of oligomers present in the prime epoxy resin(s) that can have an adverse effect on the finished composite should be included.

2. The use of existing techniques to determine the major components in the matrix formulation should be expanded and the test methods standardized by round-robin testing. Accept/reject limits should be refined by testing of composites made from prepregs with known discrepancies in purity and chemical composition. Finally, rheology property test methods allowing quantitative definition of the response of a prepreg to a given cure cycle should be developed and processibility acceptance criteria should be established.

3. The effects of bulk and surface impurities and surface morphology on fiber properties should be investigated along with the effects of various surface treatments and sizing on fiber properties, their compatibility with matrix resins, their contributions to the fiber-to-resin interface properties, and their effects on properties of the composite.

Matrix Properties

Conclusions

1. The development of matrix materials has been mostly by empirical methods. The industry uses proprietary formulations of relatively impure chemicals in empirical cure cycles. There is a tendency to use a limited number of rather arbitrary formulations.

2. The polymer science of thermosetting matrix materials has been neglected in comparison with that of thermoplastic materials. The reason lies in the stringent conditions required for linear versus network polymerization reactions.

3. Powerful capabilities for research have arisen recently as a result of the advent of new separation techniques (e.g., preparative liquid chromatography) and advanced analytical techniques (e.g., Fourier transform IR).

4. An intellectual framework exists in the temperature/time transformation state diagram for understanding the relationships of the process of cure to the properties of the cured state.

5. The scientific basis of ultimate behavior (fracture and aging) is not well developed.

6. The scientific basis of fiber/matrix interactions is not well developed.

Recommendations

1. Because of the newly available separation and analytical techniques, all future basic research should use model systems to obtain a better understanding of the influence of chemistry on material properties.

2. Molecular structure and macroscopic property relationships should be the theme for developing the polymer science of thermosetting matrix materials. Numerous powerful nondestructive techniques are available and should be applied for this purpose.

3. Relationships between the process of cure and properties of the cured state should be investigated.

4. Fracture-initiating processes and toughening mechanisms should be investigated.

5. Time effects caused by physical (including fatigue) and chemical aging should be investigated, and accelerated testing methods should be developed.

6. The effects of water vapor and other physical and chemical environments should be investigated.
7. Fiber/polymer interactive phenomena should be isolated.
8. A set of desirable matrix properties should be defined for predicting, in conjunction with fiber properties, the properties of the composite.
9. Tests on unfilled matrix material should be designed that translate directly to useful data on the composite.

Fabrication of Composite Components

Conclusions

1. The properties of composite structures are sensitive to the details of the fabrication process. This correlation, however, is not well established.
2. There are no well-established curing procedures for various prepregs and various part dimensions, such as thick laminates.
3. Despite the introduction of automated equipment, composite fabrication still requires skilled labor and careful quality control.

Recommendations

1. The relationship between various prepreg and processing variables and properties of the finished part should be studied. This should include the relationship between curing cycle and residual stresses and the influence of residual stresses on the behavior of the composite.
2. There is need for more automation in all stages of fabrication, prepreg inspection, prepreg cutting and trimming, and lay-up. This includes the use of alternate material forms, such as sheets preplied by the prepreg manufacturer.
3. Materials and procedures in the bagging and sealing operation can be improved with the introduction of reusable bags, or spray-on-bags.
4. On-line monitoring of the degree of cure should be used with automatic feedback controls. This can include on-line monitoring of outgassing and the correlation with chemical and mechanical changes.
5. More science-based optimized curing procedures that can accommodate variations in component thickness and configuration and can control residual stresses need to be developed.

6. Automated quality control procedures must be established from inspection of incoming materials, through lay-up, curing monitoring and control, and nondestructive evaluation of the finished part.

Unidirectional Ply Properties

Conclusions

1. Currently, only very selected properties of the unidirectional ply (the basic building block from which a composite structure is constructed) are experimentally characterized routinely.

2. More sophisticated design requirements are rapidly requiring more complete characterization of the unidirectional ply. Examples include temperature and moisture effects, impact, viscoelastic response, damping capacity, fatigue behavior, and determination of failure modes.

3. Complete experimental characterization of even the mechanical properties of the unidirectional ply, for each fiber and matrix combination, fiber volume, etc., is expensive, but desirable.

4. Analytical methods of predicting unidirectional ply properties are becoming more accurate and reliable. These micromechanical analyses permit the study of compositional variations with relatively little effort and expense by making a series of routine computer runs.

Recommendations

1. The continued development of test methods suitable for characterizing the unidirectional ply properties of organic matrix composites should be encouraged.

2. Emphasis should be placed on the selection for complete characterization of a few composite material systems to be established as standards.

3. Theoretical analyses should be further developed and presented in forms convenient for general use.

4. Emphasis should be placed on the development of additional micromechanical analyses and related computer programs emphasizing rigorous approaches and encouraging developments in relatively unexplored areas such as environmental effects, viscoelastic response, dynamic loading, fracture mechanics, and failure mechanisms.

5. Fracture studies using experimental techniques such as scanning electron microscopy to identify fracture initiation and failure modes should be encouraged.

Design and Analysis

Conclusions

1. For a reasonably simple load history and service environment, existing techniques can adequately predict, for design purposes, laminate stresses and deformations when ply properties are known.

2. Available failure analyses do not adequately predict laminate ultimate behavior in a number of modes important for design: static compression and shear; flaw sensitivity; fatigue and strength reduction by time, temperature, and moisture. This weakness reflects a basic ignorance of failure mechanisms for composites.

Recommendation

Theoretical models and experimental studies should address laminate failure with emphasis on uncovering the basic mechanisms that control failure and on developing predictive techniques for designers. Studies should be directed at compression and shear failure, fatigue, fracture toughness (flaw sensitivity), and prediction of laminate failure resulting from the synergistic effect of sustained loading, elevated temperature, and high humidity.

Predictive Life Tests and Accelerated Testing

Conclusions

1. The proper characterization of organic matrix composites includes determination of the behavior of the material over its anticipated or extended life. Because polymeric systems are subject to various rate processes that alter properties of these materials, it is necessary to develop methodology (including the development of rate models for the various phenomena that alter material properties or performance) that will allow for long-term characterization.

2. The models for statistics of failure of composite materials do not now model source of variability. Furthermore, no comprehensive treatment is available that allows for either multiple failure modes and processes, or synergism of processes.

3. The models of kinetic phenomena in composite materials are in an early stage of development. Models for the phenomena are modeled independently, yet interactions among diffusional, reaction,

physical and mechanical phenomena are extremely important in determining life.

4. No coherent methodology has been developed for accelerated life testing of composite structures.

Recommendations

1. The most significant need in the field of prediction of the life of organic matrix composite structures is the development of synergistic rate models that account for the interaction of material deformation, damage, stress, and environmental parameters. A great deal of fundamental work is required in this area.

2. Kinetic models of polymeric aging resulting from temperature, stress, fatigue, and diffusion are required for these material systems. In particular,

    - physical aging models must be developed to describe spontaneous enthalpic relaxation-induced consolidation and embrittlement of the polymer, and

    - chemical rate and diffusional models of decomposition reactions caused by service environments are required.

3. Methodologies that produce accelerated degradation rates must be developed such that the structure can be tested to several lifetimes in a time frame less than real time.

4. Fatigue models that utilize accelerated load and environment spectra to evaluate structural life should be developed and validated.

5. Comprehensive models of material variability that account for multiple failure modes and model source of variability must be developed.

Nondestructive Evaluation

Conclusions

1. Flaws in composites may be introduced during processing and fabrication, and they may be induced or enhanced in service.

2. The criticality of flaws or effects of defects on stiffness and strength, especially irregular or dispersed flaws, are not well known and understood.

3. A variety of nondestructive evaluation (NDE) techniques are applicable to composites. They include radiographic (X-ray and

neutron), holographic, thermographic, acoustic (acoustic wave, acoustic emission), photomechanical (moire and photoelastic coatings), embedded sensor, and ultrasonic techniques. The most commonly used method is ultrasonics (through-transmission, pulse echo).

Recommendations

1. Stress and strain analyses (analytical and experimental) should be conducted around realistic flaws detectable by NDE. Stress concentrations and stiffnesses should be determined as a function of flaw size and geometry.

2. Failure analyses (analytical, experimental, and semiempirical) should be conducted to correlate strength with defect size and geometry.

3. Efforts should be devoted to monitoring, understanding, and modeling flaw growth in composite structures subjected to service loading and environmental conditions.

4. Methods should be developed to estimate residual strength or residual life based on flaw-growth behavior.

5. Effects of chemical and physical matrix degradation of stiffness, strength and residual life should be studied.

6. Better communication is desired between NDE technologists and composite mechanicians.

7. Further development is needed of various NDE techniques applicable to composites with a better understanding of the advantages and limitations of each technique. Results of the various techniques should be correlated.

8. Specimens with realistic "standard" or "reference" flaws are needed for system calibration.

9. There is need for further development of portable equipment and techniques for field inspection of composite structures and for the elimination of subjectivity from such measurements.

10. Reliable techniques are needed for detecting dispersed types of flaws such as moisture absorption and matrix degradation.

CHAPTER I

INTRODUCTION

The use of organic matrix advanced composites as primary (system critical) structures has increased rapidly. These materials have appeared in a number of sophisticated, expensive hardware applications central to our national capability in defense and aerospace systems. The intrinsically high specific stiffness and strength of these advanced composites have met the needs of the designers of high-performance systems. Their potential in lightweight, fuel-efficient cars and trucks is just beginning to be exploited.

The growth in interest and use of these materials has paralleled the development and availability of high-performance filaments. In the 1940s the principal structural reinforced plastic was E-glass polyester. This material was used as a replacement for metals, usually with very large safety margins or in noncritical structures. About 1955 S-glass[1] was employed in filament-wound rocket motor cases; marking the first use of reinforced resin as a primary structure. For these applications epoxy replaced polyester as the matrix material. Although light and strong, S-glass composites exhibited rather low stiffness and poor fatigue characteristics. The advent of boron monofilament around 1960 provided aircraft manufacturers with the requisite stiffness and fatigue resistance to redesign and replace aluminum airframe components. Carbon and graphite fibers, which became available commercially around 1965, exhibited adequate strength and stiffness for aerospace designs and proved to be more economical and processible than boron. The latest fiber development (about 1970) was that of the organic-based aramids. Because of the very high specific tensile strength of these materials they were selected for motor case windings and containment vessels.

The predominant matrix material for most of these advanced composites continues to be some form of epoxide resin. The development of new fibers has not been matched by the introduction of new resins. Most of the formulations in use today are materials synthesized and marketed in the 1950s and 1960s.

In contrast to the more commonly used structural materials, particularly metallic alloys, the development and use of composites as structural materials has been relatively recent. As a consequence, there

---

[1] S-glass was developed for use with aircraft components and missiles. Although it is more expensive to produce, it offers strength-to-weight ratios in excess of most metals. S-glass has a higher tensile strength and modulus of elasticity than E-glass (electrical glass fiber).

has not been the opportunity to develop either the broad experience or technology base to use these composites with the same degree of confidence.

The first objective of this study is to survey and assess the state of the art of organic matrix structural composites technology to determine a rational path toward building this degree of confidence. The second goal is to formulate a set of recommendations designed to

(1) Assure by prior specification that fabricated structures will meet performance requirements;

(2) Predict lifetime behavior through analysis and accelerated test methods; and

(3) Provide verification methods for both, thus assuring product specification, and early indication of failure.

The report limits its concern to those advanced composite systems that are in wide use or appear to have the greatest potential for high-performance application. These composites are the continuous-filament, high-modulus, high-strength fibers (S-glass, boron, graphite, and aramid) contained in glassy polymer resin systems (epoxy, polyimide, and polyester). The reinforcing fibers are initially supplied in the form of monofilament (boron), roving (glass), tows (graphite), yarn (aramid), cloth, or mat. The resin matrix is formulated to contain the basic polymer, hardener, additives, and diluents. The most commonly used resins are epoxies; however, in some applications polyimides and polyesters are used.

During composite fabrication, layers of prepreg tape (or wet lay-up) are stacked to form the desired three-dimensional shape along prescribed orientations, producing a laminate reinforced in one or more directions. The lay-up is typically covered with a separator and bleeder cloths, bagged, and then cured in an autoclave under pressure and vacuum following a prescribed cure cycle. In some fiber-winding processes the lay-up is cured on the mandrel by application of the temperature cycle alone. The finished part may be further machined or bonded to some other part as required in the structural application. Because of the sensitivity of the final material properties to process history, all the above processes (handling of the materials, prepregging, lay-up, curing, and machining) affect or determine the intrinsic properties of the finished part.

The advent of advanced composites has afforded designers a class of materials with exciting possibilities. However, along with their potential, composites have exhibited certain problems that have become more apparent as performance demands increased and safety margins decreased. These problems fall generically into two related categories. The first is variation in properties, both in precursor materials and final composite. The second in an inability to predict the effect of material variation, flaws, and environment on strength and life. The second category also raises concerns about the inability to predict behavior of a structural material subjected to a combination of effects (such as moisture, temperature, and sustained load).

There are many supply sources, manufacturers, and processing steps necessary to produce a composite part. The fabrication of a composite laminate consists of combining a substantial number of raw materials in a step-by-step process to achieve the design goal. Precursor materials are usually made to supplier rather than user specifications. In other steps of the process, the situation is different: proprietary formulations and practices are often employed. A large proportion of properties of the final part are developed during the latter stages of part manufacture. As a result, the properties of composites are sensitive to the details of each of the successive process steps. This can result in different final properties for essentially similar precursor starting materials.

Composites are susceptible to a variety of failure modes and are more sensitive to temperature and environment than most structural metals. The combined effect of stress, temperature, time, and environment can accelerate failure synergistically. Because flaw growth and toughness in laminates are phenomena that are not well understood, composites are often grossly overspecified or else improperly designed using conventional metal design practice.

With the already-known material peculiarities and problems discussed in this chapter in mind, the committee undertook the task of assessing the composite field. The organizational structure of the study followed the lines of those elements that, if properly and completely understood, would assure the attainment of the objectives stated earlier in this chapter.

CHAPTER II

STARTING COMPONENTS

Starting components for composite materials have been defined by the committee to be (1) the raw materials used in the preparation of the matrix resin, (2) the formulated resin, (3) the reinforcing fiber, and (4) the finished prepreg from (2) and (3).

The purpose of this chapter is to discuss the characterization of these components. Current characterization procedures will be reviewed, and needed improvements in methodology will be recommended for the following major systems:

1. Matrix resins: epoxies and polyimides;
2. Fibers: carbon[1], boron, glass, and aramid; and
3. Prepregs: unidirectional tape formed by impregnation of the fibers with the resins.

Carbon reinforced epoxy systems are emphasized in this chapter because of their extensive current and potential use.

MATRIX RESINS

Epoxy Formulations

Epoxy formulations are used extensively in state-of-the-art structural composites. Consequently, they have received the most attention in efforts directed toward chemical characterization and quality control. The major components in the formulation of epoxy resin matrix systems include unreacted epoxies, curing agents, accelerators, tougheners (flexibilizers), and fillers.

Raw Materials

Unreacted Epoxy

Polyfunctional aryl epoxies of the type listed in Carpenter and Bartels (1975) are typical of those commercially available resins suitable for the formulation of 121°C (250°F) and 177°C (350°F) curing prepregs. Tetraglycidylmethylene dianiline (TGMDA) is a principal epoxy starting material for the matrix resin of many epoxy prepregs and

---

[1] The word "carbon" is used in this chapter in a generic sense to include all fibers produced by carbonization of precursor materials without regard to the degree of graphitization achieved in the process.

exhibits the general characterization requirements common to all epoxy raw materials. It is available commercially from Ciba-Geigy as Araldite MY 720.

Figure II-1 shows the simplified reaction for the manufacture of MY 720. Epichlorohydrin is reacted wth methylene dianiline to form an intermediate compound that is dehydrohalogenated to give the product. Ideally, this reaction would yield pure TGMDA. In actual practice, a number of other species of higher molecular weight are formed. These are believed to consist of linear oligomers (e.g., dimers and trimers), cyclic oligomers, and homopolymers. Furthermore, the following impurities are found: glycols, hydrolyzable chlorides, and water, as well as ionic components such as incompletely removed sodium chloride and sodium hydroxide. As a result, the ideal TGMDA product typically constitutes about 75 percent of the major raw material, a percent that varies from batch to batch. This variability in raw material complicates the chemical and behavioral control of the derived products, i.e., formulated resins and prepregs.

The higher molecular weight oligomers are reactive and similar in structure to the monomer. When present, therefore, at acceptable and controlled levels, they should not greatly decrease the strength, durability, and the other desirable properties of the cured matrix resin. This contention is supported by work now being conducted (Borstell, 1979; Chen, 1980; McGann, 1980; Sewell, 1981). These investigations include comparisons of the processibility, mechanical properties, and moisture sensitivity of a number of resins in which the amounts of oligomers present in the starting epoxy were varied within specified limits by selecting from a range of starting viscosities. These studies have not been completed, but early results indicate that satisfactory mechanical properties can be obtained from finished composites tested in matrix critical modes at ambient and elevated temperatures if the specimens are processed to obtain nonporous laminates of acceptably cured resin content. The programs have also shown that the major effect of resin variation is on the in-process behavioral response (processibility) of the prepreg. Therefore, the concern related to variations in oligomer content is in the production of variable thickness parts, where a change in flow for a fixed cure cycle can produce porous part or parts that are either too thick (resin rich) or too thin (resin poor).

Saponifiable chloride impurities reduce the epoxy value and, together with ionic chlorides, affect the dielectric constant of the resin. This effect on dielectric properties is of particular concern in the production of printed circuit boards; however, the chloride level required to produce adverse effects in structural composites has not been determined. The glycols, secondary hydroxyl groups, and water impurities are suspected of adversely affecting processibility by catalyzing the reaction and reducing total resin flow for a given cure cycle. They may also react with the oxirane group, reducing the functionality of the epoxide, with subsequent lowering of the cross-link density and glass transition temperature of the cured resin matrix.

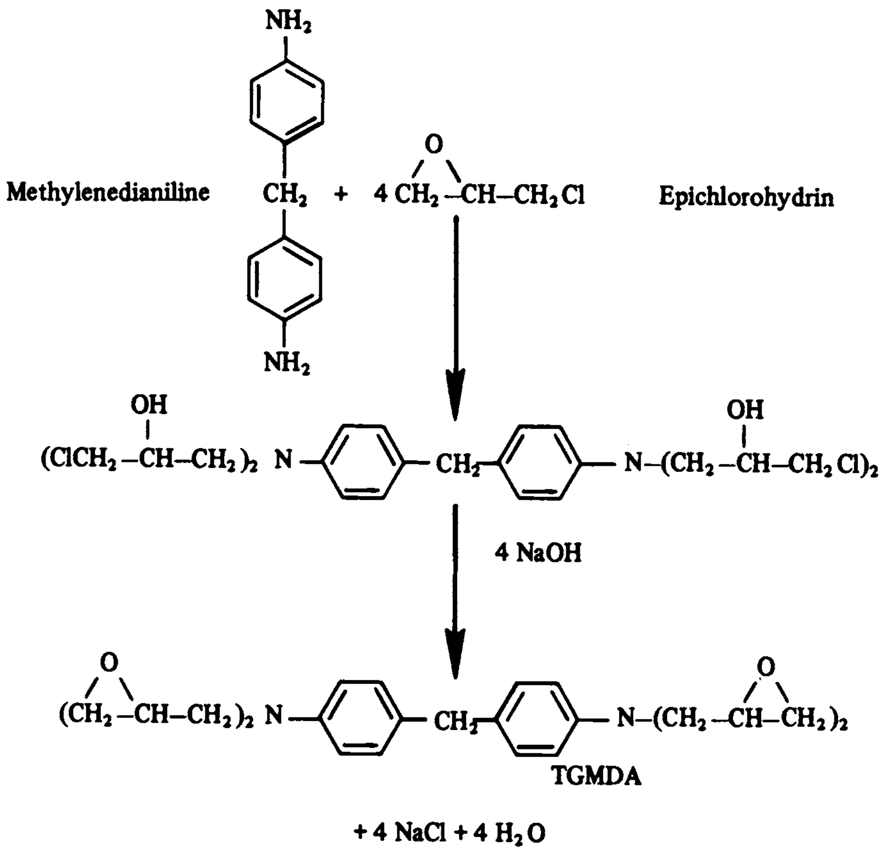


Figure II-1. Idealized reaction for production of TGMDA.

The current values from the manufacturer's specification for MY 720 are listed in Table II-1. An improved specification would include, in addition to these, gel permeation chromatography (GPC) values, which would define the molecular weight distribution by ratios of the peak heights of the higher molecular weight species to that of the TGMDA monomer. Reverse-phase liquid-liquid chromatographic (RPLLC) separations, based on differences in component polarity, would further enhance control. As many as 15 or 20 different impurities or species, other than the TGMDA monomer, have been found by this method.

TABLE II-1 Ciba Specification for Araldite MY 720

Parameter	Specified Value	Typical Value
Epoxy value, equivalents/100 g (0.22 lb)	0.75-0.85	0.79-0.82
Epoxy equivalent weight	117-133	122-127
Viscosity at 50°C (122°F), centipoise	35,000 max	10-15,000
Hydrolyzable chlorine, %	0.53 max	0.15-0.50
Ionic chlorides, ppm	300	7-12
Acetone insolubles, ppm	500	10-100
Volatiles, %	<1%	<0.2%

It would not be possible to vary these individual species in quantities sufficient to examine their effect on prepreg processibility or composite mechanical properties; however, their characterization would be valuable background information available for troubleshooting and comparing TGMDA from varied sources. Reaction rate comparisons have also been suggested for batch control of the major epoxy used for a resin matrix formula. This could be accomplished for TGMDA by rheological measurements under fixed time and temperature parameters for a mixture containing 25 percent by weight of a purified standard diaminodiphenyl sulfone (DDS) curing agent.

Curing Agents

A curing agent common to many commercial epoxy formulations used for carbon-fiber prepreg is DDS. Dicyandiamide (DICY) is another curing agent suitable for many epoxy resin formulations. It is found mainly in resin formulations in which the larger diameter fibers, such as boron and glass, are used. DICY and DDS are established commercial products. Typical specifications for commercially available DDS and DICY are given in Table II-2. The tests are considered adequate to characterize these curing agents; however, the limits can and should be tightened. For example, melting point ranges are so broad that they allow the presence of substantial impurities. The resin formulator should apply statistical methods to receiving inspection data and adjust the acceptance limits accordingly. If purchased by the formulator on the basis of vendor certification, the formulator should require the actual test values and negotiate specifications indicated by the statistical evaluation.

Table II-2 Typical Specifications for DDS and DICY

Test	DDS	DICY
Melting point, °C (°F)	170-180 (338-356)	200-215 (392-419)
Assay, wt%	98	-
Water content, wt%	≤ 1	≤ 1
Particle size, wt% retained on a 200-mesh screen	-	20% max.

Fillers

Fillers are seldom used as raw materials in the carbon-fiber matrix formulations but may be used in resin formulations for the larger diameter reinforcing fibers. Silicate types, such as asbestos and CAB-O-SIL, are the most commonly used. They are used mainly as a dispersion aid for the finely divided insoluble curing agents (e.g., DICY) or for flow control. Some needlelike fillers could conceivably improve the handleability of the uncured prepreg by imparting greater wet strength. Prepregs with poor wet strength cause problems during lay-up due to tape separations parallel to the fiber direction. For the small weight-percent additions, the chemical purity of available fillers is considered adequate. A specification pertaining to particle size distribution and morphology of fillers used for structural adhesives is needed; however, for composite resin matrix applications, the requirement could be limited to identification and a particle size maximum.

Toughening Agents

Elastomers, such as carboxy-terminated butadiene-acrylonitriles (CTBN), have been used to increase the toughness of matrix formulations. Another family of tougheners consists of the high-molecular-weight phenoxies. For carbon reinforced epoxy matrices, however, it is more common to add a minor amount of a second epoxy of suitable structure to improve the toughness of the cured resin. Adequate characterization of the CTBN elastomers, such as the B. F. Goodrich Hycar series, can be achieved by control of viscosity, percent carboxyl, and acrylonitrile content. Various phenoxy resins are obtainable from Union Carbide; little is known regarding a need for their characterization. If a minor epoxy is used as a toughener, it should be characterized by the same criteria as described for the major epoxy raw material component.

Accelerators

Epoxy accelerators include boron trifluoride amine complexes, triphenylphosphine, and urea derivatives such as 4-chlorophenyl-1, 1-dimethylurea (MONURON), and 3,4-dichlorophenyl -1,1-dimethylurea (DIURON). The need for quality assurance beyond the supplier's specifications has not been established.

Resins and Prepregs

The controlled processing of the raw materials to the B-staged neat resin and final production of prepreg are the responsibility of the vendor. The order and means of combining the raw materials, the time/temperature profiles, and the other processing parameters required to produce the resins are often vendor certification proprietary information. The techniques of prepregging are also often considered proprietary.

At this stage, the characterization and control of prepreg becomes a joint effort of the vendor and the composite fabricator. Typical of the conventional receiving inspection and vendor certification tests for the prepreg are physical tests (such as resin content, volatiles, tack, flow, prepreg drape, and fiber areal weight) and laminate mechanical property tests (including interlaminar shear, longitudinal tensile strength and modulus, transverse tensile strength and strain, and longitudinal compression strength and modulus).

For purposes of discussing the physicochemical characterization and in-process behavioral control tests needed for the finished resin and prepreg, the following hypothetical epoxy resin formulation may be assumed:

	Wt%
Major epoxide (TGMDA)	65
Minor epoxide (epoxy cresol novolak)	10
Curing agent (DDS)	24
Accelerator (BF_3 complex)	1

Optimum characterization of the B-staged and prepreg resins requires the following procedures:

Procedure	Component or Condition
Reverse phase liquid-liquid chromatography (RPLLC) and infrared (IR)	Major and minor epoxides, curing agent, reaction products
Atomic absorption (AA)	Accelerator
Differential scanning calorimetry (DSC)	Accelerator, thermal history
Gas chromatography (GC)	Moisture
Standard wet methods	Impurities (Cl, OH, and epoxy equivalent weight)
Viscoelastic profiles (time/temperature)	Rheology and processibility

Tests for the total weight percents of the epoxides and curing agents are necessary to verify that the correct starting weights were used. The weight percents for the unreacted (free) epoxides and curing agent together with the identified reaction products are necessary to determine the effects of subcomponent and final B-staging process operations.

The accelerator concentration is based on a boron determination by AA. Also, epoxy formulations containing a BF_3 complex show a DSC curve with major and minor peaks. The initial peak (minor) is associated with the accelerator, and the ratio of peak heights, for a given heating rate, may be used to verify the presence and concentration of the BF_3 complex. The DSC thermogram gives a curve that is unique to different formulation variables and component concentrations; however, its value in system characterization varies wih the complexity and type of formulation.

Rheological measurements defining the viscosity as a function of time and temperature are necessary for adequate behavioral control of the material. These measurements establish that a given batch of prepreg will have proper flow characteristics and will process in the same manner as the batches used to optimize the fabricator's cure cycle. This is emerging as an area of substantial research endeavor. Weight percents for the unreacted (free) amounts of epoxies and curing agent together with the concentrations of the reaction products are also useful for this purpose; however, the results of these determinations are not entirely definitive because some resins receive a varied final B-stage cooking time (based on the viscosity of the major epoxy starting material) to give a final prepreg product that has consistent drape and tack. Other resin systems are manufactured using fixed time/temperature formulating parameters, and the tack and drape vary over a wider range.

Polyimide Formulations

The need for improved thermal and oxidation resistance has led to the development of many high-temperature-resistant polymers. In the course of these developments, polyimides (PIs) have emerged as the predominantly used high-temperature-resistant polymer system for applications requiring extended use at temperatures exceeding 200°C (392°F).

Two classes are of importance: linear, condensation PIs and cross-linked, addition PIs. The basic imide chemistry is the same for both types and requires a tetracarboxylic acid or derivative and a diamine. A variety of tetracids, anhydrides, esters, and diamines have been employed (Adrova et al., 1970). Condensation PIs form linear polymers having high molecular weights. Addition-type PIs, however, contain a third monomer ingredient that terminates the imide chains to form oligomers of low molecular weight that are cured by addition reactions of the functionalities on the chain terminating groups to form highly cross-linked structures (Gibbs and Breder, 1975; Dexter and Davis, 1979; Serafini et al., 1972; St. Clair and Jewell, 1976, 1978). One significant characteristic of the imidization reaction is that precise stoichiometry is required for the achievement of the optimal chain length during polymerization.

Raw Materials

The basic raw materials for most commercial polyimides exhibit very good potential for straightforward chemical characterization. They are, typically monomers or short chain oligomers having relatively low molecular weights and, as a consequence, can be characterized by simple physical and chemical techniques. Typical monomers are shown in Figure II-2. Anhydrides and tetracids can be assayed by traditional wet chemical techniques, melting point range, and spectroscopic analyses. Most commercial grades appear to be adequate for use in the current resin compositions. However, to guarantee correct stoichiometry, the bulk reagent should be assayed. Diacid-diesters are prepared by refluxing the respective anhydride in alcohol. In general, it is desirable to prepare

Figure II-2

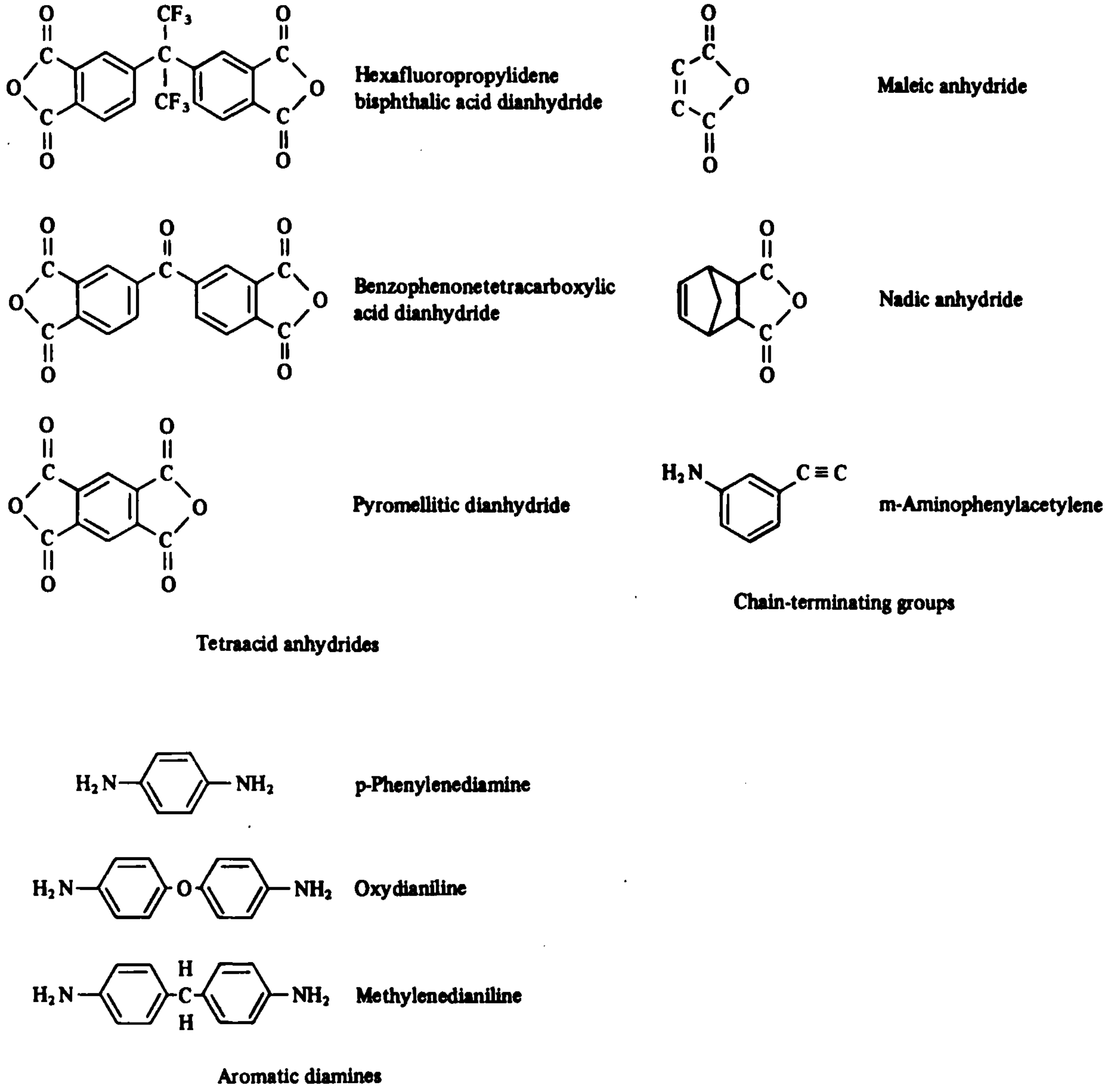


Figure II-2. Polyimide matrix raw materials.

fresh solutions for each resin batch and to store them at subambient temperature. Exposure of these solutions to extensive reflux or excessive heat during reaction or to extended ambient storage permits the formation of higher ester (triester and tetraester) impurities, which can cause variability in resin processing and in composite properties. The ester solutions can be readily assayed using liquid chromatography or spectral techniques.

Aromatic diamines are available commercially in several grades that can vary significantly in impurity level and type and in isomer content. Many of these variables can affect the processibility and final properties of the polymer. The amine content can be assayed using traditional wet chemical methods and chromatography. The isomer content in many aromatic amines can be determined spectroscopically or chromatographically. The isomer mix may be most significant in resin systems employing phenylenediamine where the meta isomer content is often increased to enhance solubility and to lower the melt temperature of the polymer. The use of polyamines introduces an additional variable. The molecular weight distribution of the polyamine may vary as well as the amine content. This additional variable is most easily monitored by liquid chromatography.

Reactive chain-terminating monomers are amenable to all the traditional modes of characterization. Each reagent will potentially have unique criteria for purity and reactivity.

Overall, the principal concern in choosing and characterizing the acids, amines, and chain-terminating monomers is the definition of a known and reproducible level of purity for the available raw materials so that the stoichiometry required for complete imide formation can be attained. To date, the use of explicit chemical criteria for material acceptance has not been fully implemented.

Many of the commercial imide resin systems are prepared or dispersed in solution. Some of the solvents used are dimethylformamide, N-methylpyrrolidinone, ethanol, and methanol. Generally, the resin systems that have the higher degree of polymerization require the more powerful solvents (such as dimethylformamide), while resins consisting of monomers or oligomers of low molecular weight employ the solvents having lower boiling points. The principal point of concern is to avoid reactive stabilizers, denaturants, or impurities in the solvents that might interfere with the imide chemistry. Solvent purity can readily be monitored chromatographically.

In general, accelerators, tougheners (flexibilizers), fillers, and other modifiers have not been incorporated in the commercially available imide systems.

Resins and Prepregs

The basic requirements for characterizing PI resins and prepregs are analogous to those for epoxies. The approaches and techniques that have been employed are essentially the same. It is necessary to have a methodology that provides compositional data including impurities and a measurement of the degree of advancement. Liquid chromatrography is the most commonly employed technique for such tests. Both GPC and RPLLC have been successfuly applied. To date, however, no single approach has been defined as generally applicable.

Several quantitative aspects of these resins and prepregs can be monitored, and, depending on the criticality of the application, the following should be documented: stoichiometry, degree of advancement, impurities, and prepreg composition.

Stoichiometry

Careful chromatographic or spectral analysis can indicate the relative (or, if desired, the absolute) concentration of components in most PI resins and prepreg extracts. The principal difficulty lies in accounting for partially reacted material, but this can be done in many cases.

Degree of Advancement

The amount of prereaction (in most cases amide or imide formation) appears to be one of the more critical variables in the imide resin systems. This is probably because the stiffness of the imide chain causes significant changes in properties such as melt temperature and resin viscosity at fairly low levels of imidization, and such physical changes can markedly affect the material response during processing. Unfortunately, this aspect of the resin appears somewhat difficult to control in many resin systems. The conditions used for large-scale resin mixing and prepregging can lead to significant and variable advancement of the resins. Liquid chromatography, particularly the size exclusion mode, is most amenable to the analysis of the oligomers of interest for most imide systems, and a reasonably detailed analysis of the results may be required to characterize the degree of advancement of the resin of interest.

Impurities

Any impurities or intermediates that have a known or suspected undesirable affect on resin processing or final properties should be quantified and, limits should be defined. For example, triester and tetraester impurities that have been observed in ester monomer solutions can also be detected, in some cases, in resin solutions. Liquid chromatography is the method of choice for both the identification and the quantification of such soluble impurities. Of course, not all impurities will be soluble or be conveniently separated chromatographically. Such analyses require more specific physical or chemical techniques.

Prepreg Composition

The resin-to-fiber ratio and the net solvent content are both critical factors in the handleability and processability of prepreg;

consequently, both should be measured. It is important that the vendor and the fabricator arrive at a mutually agreeable procedure for these tests to remove potential ambiguities caused by residual solvent, partial imidization, moisture pickup, and other factors related to the chemistry of the imides.

Other Resin Systems

Polyesters (Unsaturated)

The laminating polyester resins are typically prepared from a variety of dibasic acids and polyhydric alcohols that are dissolved in a reactive monomer such as styrene. Diluents include toluene, methyl methacrylate, and diallyl phthalate. Peroxide catalysts and heat are used to produce the rigid cross-linked structure. Polyester reinforced with glass fiber accounts for the largest volume of prepregs. To date, the applications suitable for unsaturated polyester composites have not been in highly critical structural areas, and traditional mechanical property and performance type testing is considered adequate for characterization and control.

Phenolics

Phenolic resins are derived from the condensation of phenols and aldehydes. Because water is eliminated during the condensation, it is more difficult to process prepregs using phenolic matrices. Phenolics did, however, find early use in missile applications. The most successful uses have been in ablatives with applications having a transient heating environment involving very high temperatures but short-time structural requirements. Chemical characterization and compositional controls of the finished resins and prepregs were not developed and implemented and probably will not be because most of the early applications have given way to improved epoxy formulations that are more easily processed and have superior strength properties.

Thermoplastics

The use of thermoplastic resins as matrices for high-performance composites is relatively new. Nylon, polysulfone, poly(phenylene sulfide) and poly(butylene terephthalate) are likely candidates for automotive as well as aerospace applications. Thermoplastics are rigid, strong, and can be thermoformed easily. However, they require high processing temperatures and pressures and are in general susceptible to solvent attack. Poly(phenylene sulfide), on the other hand, is exceptionally resistant to any solvents below a temperature of 204°C (400°F); its mechanical properties are good to 121°C (250°F). Development of physicochemical methods for quality control of thermoplastics should occur concurrently with the development of their structural applications.

REINFORCING FIBERS

The major reinforcing fibers and their general performance characteristics are given in Table II-3. Mechanical and performance tests for the fibers or for laminates prepared from a standard matrix are currently used as acceptance criteria. This section discusses the extension of these current methods to include characterization tests that specifically address the intrinsic properties of the fibers. Properties to be considered are the bulk properties, such as crystallinity, impurities, size, shape, and fracture mode, as well as properties that include the morphology and chemistry of the fiber surface.

Carbon

Acceptance criteria for composite prepreg require that control of the reinforcing fibers be enhanced beyond current performance tests. The testing required to control the intrinsic properties of carbon fibers is brought into focus by the general processing steps involved, as shown in Figure II-3. The properties of the polyacrylonitrile precursor and the processing parameters of carbonization/graphitization steps are largely responsible for the bulk properties of the fiber. The surface of the carbon fibers must be treated to obtain proper wetting by the matrix resins and to obtain acceptable fiber-to-matrix compatibility and adherence. This is achieved with gaseous oxidation either with oxygen, water vapor, ammonia, or a halogen, or by liquid oxidation with such agents as hydrogen peroxide, sulfuric acid/dichromate, sodium hypochlorite, sodium hydroxide, or phosphoric acid. Time, temperature, and concentration are rigidly controlled. In some cases involving liquid oxidation, electrolysis is required.

In addition to the surface treatment, some carbon fibers are given an additional finish or sizing, amounting to about 1 percent by weight of the fiber. The sizing is added mainly for ease in handling the fiber and must be compatible with the matrix resin.

The treated-fiber surface and, if present, the sizing, constitute the very critical fiber-to-matrix interface and, therefore, should be controlled.

Potentially applicable tests and methods appropriate to fibers and their sizings are given in Tables II-4 and II-5.

It is recommended that the data obtained by characterization, in accordance with Tables II-4 and II-5, be evaluated and used as a basis for selecting batch control tests. As was done with the resins, the accept/reject limits for the first generation quality assurance criteria could then be established statistically by replicate testing of a number of representative fiber production batches. Second generation quality assurance requirements would require adjusting limits on the basis of differences in performance.

Table II-3 Performance Characteristics of Major Reinforcing Fibers in Comparison with Selected Materials

Material	Tensile Modulus		Tensile Strength		Specific Gravity
	GPa	10^6 psi	GPa	10^3 psi	
Glass	72-86	10.5-12.5	1.7-3.4	250-500	2.48-2.53
Aramid	60-130	9-19	2.8-3.6	400-525	1.44-2.00
Boron	360-410	53-60	2.8-3.7	400-530	2.22-2.59
Carbon (PAN-based)	180-520	27-75	1.9-3.3	270-475	1.66-1.97
Glass/epoxy laminate	39-54	5.7-7.8	1.1-1.6	160-235	2.02-2.08
Carbon/epoxy laminate	90-290	13-42	0.6-2.0	90-286	1.55-1.69
Boron/epoxy laminate	210-224	30-32.5	1.5-1.61	220-233	1.88-3.38
Aramid/epoxy laminate	43-90	6.3-13	0.76-1.4	110-200	1.35-1.40
Steel	200-207	29-30	0.5-2.0	70-300	7.75-7.92
Titanium	110	16	0.10-1.2	15-180	4.43-4.71
Aluminum	76	11	0.20-0.55	30-80	2.77-2.80

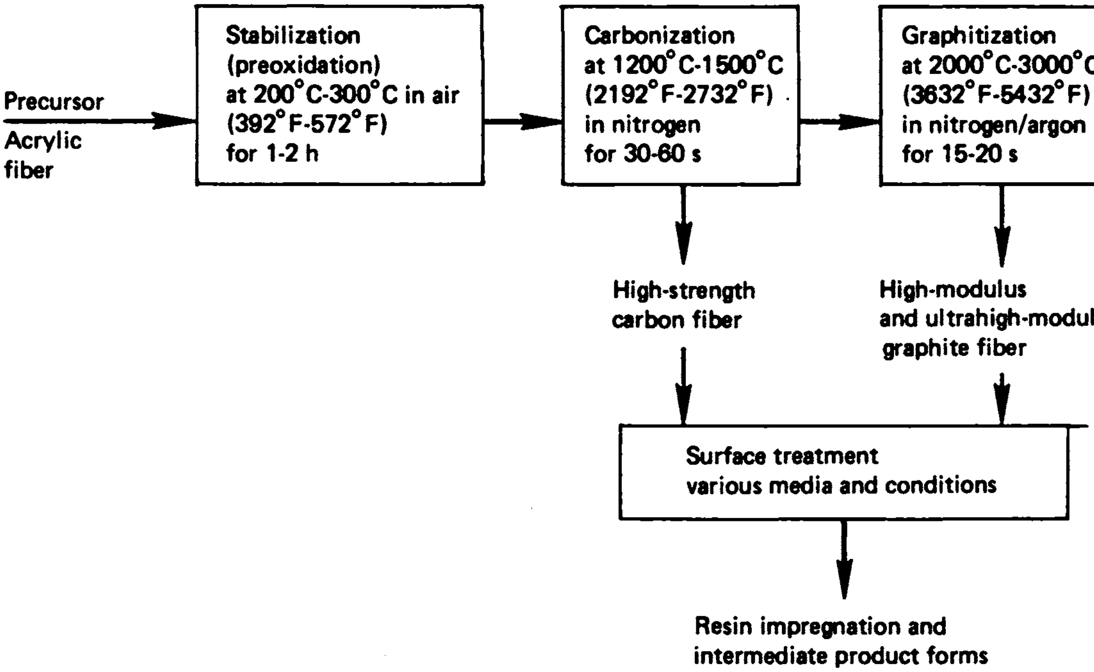


Figure II-3. Carbon fiber process.

Table II-4 Characterization of Carbon Fibers

Test	Method	Application
Surface analysis	Scanning electron microscopy	Surface morphology imperfections
Surface and bulk analysis	Energy dispersive X-ray analysis	Elemental impurities
	Emission spectroscopy	
Metallography	Optical	Shapes, size, and fracture mode
Structure	X-ray diffraction	Percent crystallinity

Table II-5 Characterization of Sizing

Test	Method	Application
Determine percent by weight	Solvent dissolution or by pyrolysis	Quality and consistent performance
Separate, identify, and analyze components	RPLLC and Fourier transform IR	Compatibility of cure with matrix resin
Perform thermal analysis of sizing and mixtures containing matrix resin	Differential scanning calorimetry	Effect of sizing on processibility and strength of matrix
Define rheology of sizing and mixtures containing matrix resin	Viscoelastic and dynamic mechanical analysis	Compatibility of processing behavior with matrix resin
Determine sizing uniformity	Microscopy	Quality and consistent performance

Boron

Most continuous boron fiber is produced by chemical vapor deposition of boron on tungsten wire. The boron is deposited on the resistance heated tungsten wire by dissociation of boron trichloride vapor in the presence of hydrogen. The typical size is a 101-μm (4.0-mil) diameter fiber with a 13-μm (0.5-mil) tungsten core. Acceptable properties are obtained without special surface treatments or finishes.

Boron-fiber production and use in structural composites predates that of the carbon fibers. Also, the production processing parameters of boron have been firmly established, whereas carbon-fiber production is still evolving. Under these circumstances, characterization and quality assurance criteria of boron fibers beyond the present state-of-the-art performance-type testing are not recommended.

Glass

Glass fibers are easily drawn from the molten state and their early availability, high-strength properties, and low prices have contributed to high-volume use. The most demanding structural use of glass-fiber-reinforced composites has been for DOD applications, particularly those of the U.S. Army for helicopter parts. The Army Materials and Mechanics Research Center has directed efforts toward improving the reliability of glass-fiber-reinforced composites through more complete characterization of the fiber and points out that the performance of the composite may well depend upon the composition of the fiber. There are technologies available to characterize the fiber and they should be pursued (Thomas et al., 1979). Environmental degradation of glass fibers is of concern because they age and lose properties rapidly after leaving the spinneret. Water is known to leach metal oxides from glass fibers. It is therefore reasonable to assume that moisture absorbed by the composite will migrate to the fiber and the soluble oxides will dissolve in the water, gradually forming pockets of salt water that could destroy the bond between the fiber and the resin. Characterization methods investigated by the Army Materials and Mechanics Research Center and suggested as a basis for future quality control criteria are as follows:

1. Chemical analysis of fiber
    a. AA
    b. Emission spectroscopy
    c. Electron spectroscopy for chemical analysis (ESCA)
    d. Wet analysis

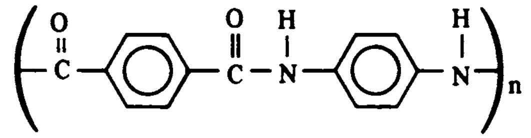
2. Chemical analysis of water leachate
    a. AA
    b. Wet analysis

3. Physical properties

In addition, the fiber finishes should be identified and controlled. Suitable methods include gas chromatography/mass spectroscopy, high-performance liquid chromatography/Fourier transform IR, and ESCA.

Aramid

The term "aramid" denotes a class of aromatic polyamides that has been developed commercially during the past 10 years. A typical aramid polymer structure is represented by the following:



Aramid fibers have been processed to a high degree of molecular orientation. The aromatic content and the high degree of orientation combine to give remarkable physical properties. The fibers are useful over a broad temperature range (nominally -196°C to 500°C [-321°F to 932°F]). They have an ultimate tensile strength of approximately 3.4 GPa (5 x 10^5 psi). Because of their relatively low density (1.44 g/cm^3 [0.83 oz/in^3]), they have a higher specific strength than any of the other fibers. They have a moderately high modulus, which is between that of glass and boron or carbon fibers. (See Table II-3). Laminate tensile properties reflect the excellent specific properties of aramid fibers. The fibers also give rise to improved impact strengths relative to more brittle reinforcements. Limitations in the use of the fiber arise primarily from its extreme anisotrophy which results in poor transverse tensile and interlaminar shear strengths and rather low longitudinal compressive strength. Its properties have led to its being used as replacement for glass-fiber composites in tensile critical applications such as rocket motor cases and pressure vessels. Other major aircraft applications are interior and exterior fairings.

Characterization and quality assurance criteria similar in scope to the approach outlined for carbon fibers are needed, but this area has not yet been addressed.

CONCLUSIONS

1. Characterization and quality control of the raw materials used to formulate the matrix resins are evolving. Physiochemical methods available to improve prepreg controls are being implemented.

2. The chemical composition of the matrix resins and their degree of advancement before and after the prepregging step can be determined by laboratory test methods already developed or feasible in the near term. However, present tests do not completely and quantitatively define the prepreg response to the parameters of composite part fabrication (processibility).

3. Fiber characterization and control and the fiber-to-resin interface have received minimal attention compared with the recent efforts and resulting progress in the characterization of the matrix resin.

RECOMMENDATIONS

1. The purity required for each of the starting raw materials should be determined, and quality controls for composite-grade raw materials established. The minor impurities and the types and amounts of oligomers present in the prime epoxy resin(s) that can have an adverse effect on the finished composite should be included.

2. The use of existing techniques to determine the major components in the matrix resin formulation should be expanded including measurement of the free and combined components and the reaction products. The data, where possible, should be expressed on a weight-percent basis. Standardized test methods, round-robin testing, and interlaboratory agreement should be established.

3. Accept/reject limits for the matrix resin formulation should be established by basing the initial acceptance criteria on statistically valid limits. Testing of composites made from prepregs with known discrepancies in purity and chemical composition should then be used to refine the accept/reject limits.

4. Rheological property test methods to allow quantitative definition of the response of a prepreg to cure cycles and to establish processibility acceptance criteria should be developed.

5. Effort should be directed toward systematic determination of the effects of bulk and surface impurities and surface morphology on fiber properties. The effects of various surface treatments and sizing on fiber properties, their compatibility with matrix resins, their contributions to the fiber-to-resin interface properties, and their effects on properties of the composite should be investigated. Test methods may then be selected and refined and accept/reject limits for characterization and control of the fibers established.

REFERENCES

Adrova, N. A., M. I. Bseeonov, L. A. Laius, and A. P. Rudakov, Polyimides--A New Class of Thermally Stable Polymers, Technomic Publishing Co., Westport, Conn., 1970.

Bortsell, H., Chemical Composition and Processing Specifications for Air Force Advanced Composite Matrix Materials, USAF Contract No. F33615-77-C-5196, September 1977 to July 1979, Final Report, AFML-TR-4166, November 1979.

Carpenter, J. F., and T. T. Bartels, Characterization and Control of Composite Prepregs and Adhesives, 7th National Society for the Advancement of Material and Process Engineering (SAMPE) Technical Conference, Materials Review '75, Albuquerque, N. M., October 14-16, 1975.

Chen, J. S., and A. B. Hunter, Development of Quality Assurance Methods for Epoxy Graphite Prepreg, NASA Langley Contract No. NAS1-15222, January 1978 to December 1980.

Dexter, H. B., and J. G. Davis, Graphite/Polyimide Composites, NASA Conference Publication 2079, Technical Symposium, Langley Research Center, Hampton, VA., February 28-March 1, 1979.

Gibbs, H. H., and C. V. Breder, "High Temperature Laminating Resins Based on Melt Fusible Polyimides," Copolymers, Polyblends and Composites, Advances in Chemistry, American Chemical Society, Washington, D.C., 142, 1975, p. 442.

Jewell, T. A., Chemical Composition and Processing Specifications for Air Force/Navy Advanced Composite Matrix Materials, USAF Contract No. F33615-78-C-5177, September 18, 1978 to April 18, 1981.

McGann, T. W., Chemical Composition and Processing Specifications for Air Force Advanced Composite Matrix Materials, USAF Contract No. F33615-77-C-5243, September 1, 1977 to August 15, 1979, Final Report, AFML-TR-4180, February 1980.

St. Clair, T. L., and R. A. Jewell, LARC-160: A new 550° Polyimide Laminating Resin," 8th National SAMPE Technical Conference, Bicentennial of Materials, Seattle, Wash., 1976, pp. 82-93.

St. Clair, T. L., and R. A. Jewell, "Solventless LARC-160 Polyimide Matrix Resins," 23rd National SAMPE Symposium and Exhibition, Selective Application of Materials for Products and Energy, Anaheim, Calif., 1978, pp. 520-527.

Serafini, T. T., P. Delvigs, and G. R. Lightsey, "Thermally Stable Polyimides from Solutions of Monomeric Reactants," *J*. *Appl*. *Sci*. *16*(4), 905-915 (1972).

Thomas, G. R., B. M. Halpin, J. F. Sprouse, G. L. Hagnauer, and R. E. Sacher, "Characterization of Epoxy Resins, Prepregs and Composites Using HPLC, FTS-IR and DSC," 24th National SAMPE Symposium and Exhibition, Los Angeles, Calif., May 8-10, 1979.

CHAPTER III

MATRIX PROPERTIES

ORGANIC POLYMERIC MATRICES--PRESENT STATE OF KNOWLEDGE

Organic matrices of the type used in composite materials reinforced with continuous filaments are formed by chemical conversion of reactive fluid to solid in the thermosetting process. (Thermoplastics are of limited use in this application because of the high viscosity of their melts.) Although thermosetting materials represent a neglected area of polymer science, research on them is important for providing a basis for the design of improved materials from correlations between molecular structure and bulk properties. A more complete understanding of the matrix, of the fiber reinforcement, and of interactions between the matrix and inclusion, will facilitate macroscopic design of composite materials. Specification criteria for quality control will evolve with the science.

The unsatisfactory scientific state of the field of thermosetting network (e.g., epoxy and unsaturated polyester) and linear semiladder (e.g., polyimide) materials, the most important organic matrix materials, results from limitations to their study. The materials are amorphous, which precludes intensive study by the diffraction and morphological techniques that are crucial for studies of crystalline and oriented materials. The materials are also infusible and insoluble and are, therefore, synthesized and fabricated in one operation. Unlike thermoplastics, their chemistry and physics are intertwined. Although intractability renders characterization difficult, it is this verycharacteristic that is the reason for their superior engineering behavior. Particularly important is the dimensional stability of composite materials under stress. This relative lack of time dependence is a consequence of the molecular network (e.g., in epoxies) or of the linear-but-stiff semiladder molecular structure (e.g., in some polyimides). In contrast, the flexible linear molecules of solid thermoplastic materials can undergo limited relative motion under stress to give creep. However, the unfilled glassy thermoset materials are brittle and have little commercial use in bulk form as structural materials. Homogeneous unreinforced specimens are often difficult to prepare for testing in a state without defects because of residual curing and thermal shrinkage stresses, bubble inclusions introduced during cure, and surface defects introduced by machining. Tests measuring properties to break of unfilled material often give great variability in data.

The current importance of composite materials has stimulated new approaches to the study of the organic matrix. Some of the problems of organic matrix materials, which pertain particularly to network-forming materials, are described briefly in the following paragraphs.

The chemical approach to the study of molecular structure and bulk property relationships in thermosets is difficult because of the ubiquitous use of impure reactants, proprietary formulations, and arbitrary curing conditions. To date, the industry has been fortunate in being able to get away with this. Thermoplastic materials could not have come about with such an approach because of the more stringent requisites for synthesizing linear systems (Flory, 1953). Even with pure reactants, the complexity and competing nature of the chemical reactions involved in synthesizing the networks would render molecular structure and bulk property correlations difficult to obtain. It is not surprising, therefore, to find a lack of interest in this chemistry by the academic community.

A major problem area arises because the relationship between cure and the cured state has been poorly understood. The oligomeric state and its transformation in the thermosetting process to the network structure have scarcely been studied. For example, in principle, if the final temperature used in cure is below the maximum glass transition temperature of the system, vitrification will occur during cure and essentially prevent further cure, thereby leaving a latently reactive system with a softening temperature equal to the temperature of cure. Such systems are used in aircraft today! On the research level, if the organic glasses represent quenched reaction products, molecular structure and bulk property relationships will not be obtainable.

Another area of concern involves the changes in properties that occur with time as a result of the nonequilibrium nature of the glassy state. Spontaneous physical aging leads to densification and so to further embrittlement (Ophir et al., 1978; Struick, 1978). Superimposed on this physical process are changes caused by slow chemical reaction of incompletely cured systems. These bear directly on the problems of long-term stability and accelerated testing methods.

Another current problem relates to the physical and chemical effects of absorption and desorption of water vapor by these polar matrix materials (Doyle et al., 1980; Morgan and O'Neal, 1978).

The function of the matrix is to distribute the applied load efficiently to the high-modulus, high-strength fibers in the composite, Unfortunately organic glasses display relatively low moduli and are brittle. The brittle character of matrix materials, therefore, invites study of fracture-initiating processes (such as brittle fracture, crazing, and cavitation), fatigue, plasticity, and toughening mechanisms. Improvements in impact behavior and toughness, which are the consequence of control of different failure mechanisms (Manzione et al., 1981b), can be obtained by changes in molecular architecture and morphology. Important work has involved incorporation of a dispersed rubber phase, the rubber being also partially solubilized in the continuous matrix material, by including reactive low-molecular-weight liquid rubbers in the reactants (Riew et al., 1976).

The next section on cure discusses key relationships between the process of cure and properties of the cured state using a generalized time/temperature/transformation state diagram that provides a framework for understanding and designing matrix materials.

CURE

Gelation and Vitrification

Gelation and vitrification are two macroscopic phenomena that are encountered as a consequence of the reactions that convert a fluid to a solid in the thermosetting process. Macroscopically, gelation is associated with a dramatic increase in viscosity and a corresponding decrease in processibility. Gelation times are usually measured rheologically, for a fixed-frequency experiment, by the time between the beginning of the reaction and the attainment of a fixed viscosity. On the molecular level, gelation corresponds to the incipient formation of branched molecules of very high molecular weight from low-molecular-weight multifunctional reactants and occurs at a critical and calculable extent of reaction for the particular reactive system (Flory, 1953). A molecular network develops by intramolecular reactions of branched molecules. (See Figure III-1.) Eventually the total mass may be only one molecule. A network structure will be a rubber (elastomer) at a given temperature if the segments between junction points of the network are flexible. If the segments are immobilized by further chemical reaction, or by cooling, the structure will change to a glassy (vitrified) state.

In thermosets, vitrification usually follows gelation and then occurs as a consequence of the increasing average size of the molecules and by the network becoming tighter through further chemical reaction (crosslinking). Vitrification can retard further reaction. The overall transformation from liquid to gel to rubber to glass caused by chemical reaction is termed "cure."

The properties of thermoset materials are intimately related to their process of formation (cure). The material properties therefore depend on the interplay among such factors as chemical reactants, their mutual solubility, viscosity prior to gelation, volatility of the reactants and byproducts, gelation, phase separation caused by polymerization, vitrification, chemical conversion, time and temperature paths of cure, and limits of thermal stability. A generalized time/temperature/transformation state diagram that is instructive for understanding some of these relationships is presented in Figure III-2 (Enns et al., 1980; Gillham, 1979, 1980, 1981b). It displays the four distinct material states encountered during cure: liquid, elastomer (gelled rubber), ungelled glass, and gelled glass.

The state diagram may be constructed by measuring the time to gelation and the time to vitrification versus the isothermal temperature of cure (T_{cure}). A convenient technique involves using a torsion pendulum in which the specimen is a substrate (e.g., glass, carbon, or aramid fibers) impregnated with the system under investigation (Gillham, 1974; Schneider and Gillham, 1980; Gillham, 1981a). Use of a supported sample permits investigation of the complete cure process versus time

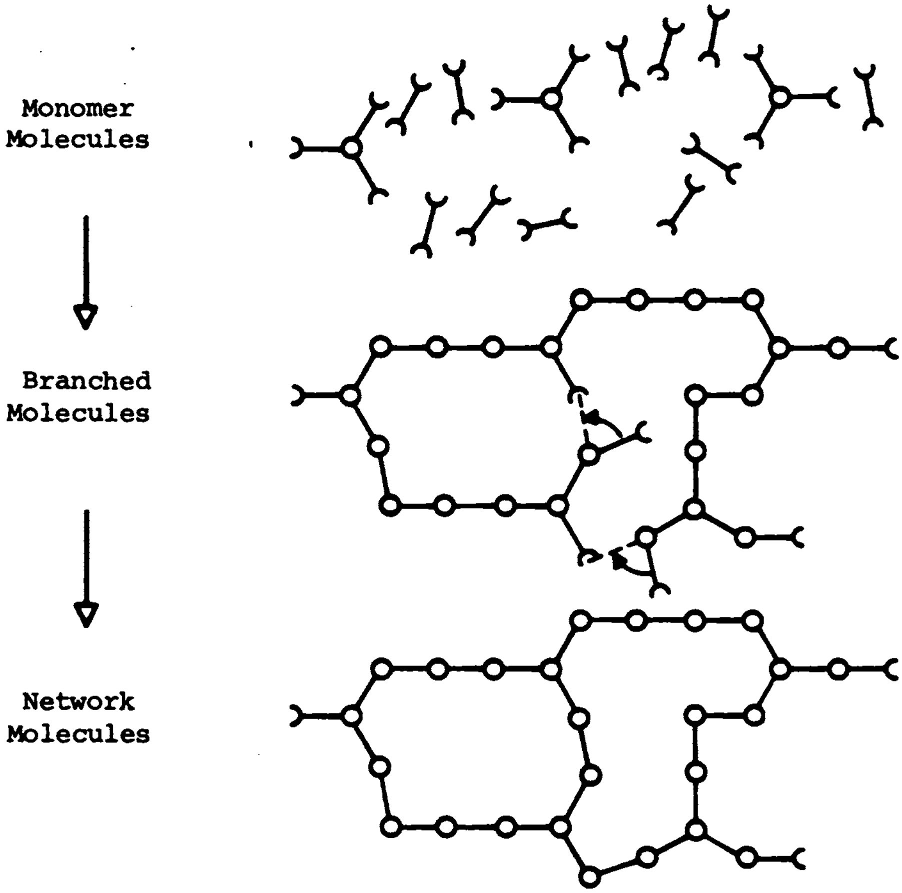


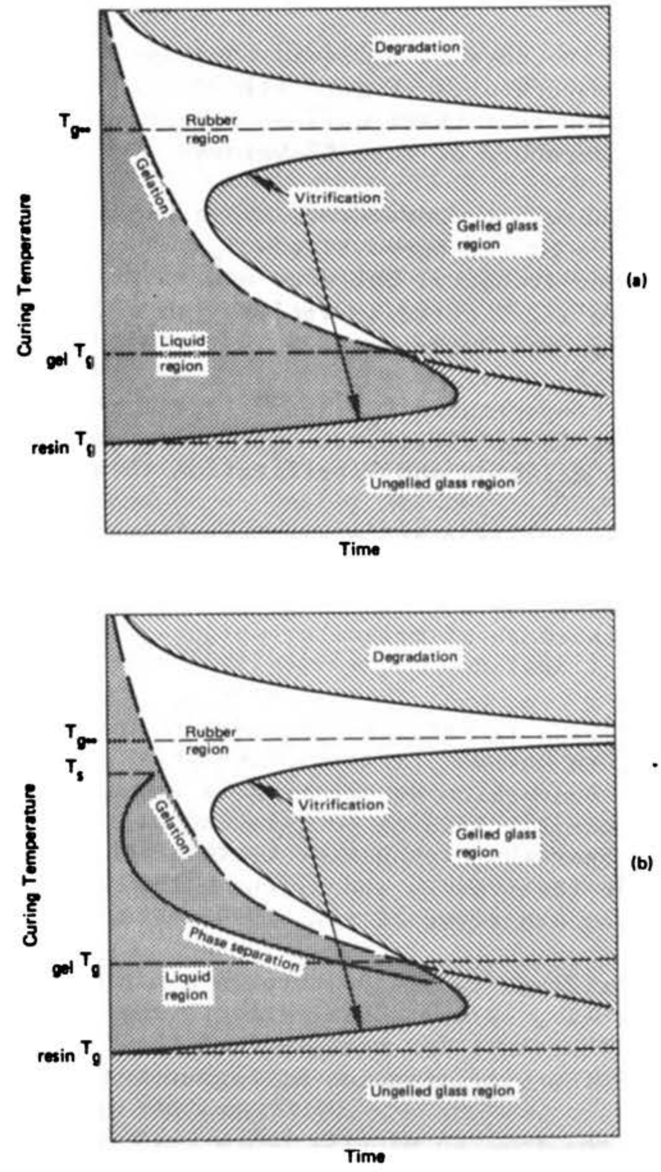
Figure III-1 The thermosetting process. Three-dimensional network polymers can be synthesized from systems containing multifunctional (more than 2) reactants. Network molecules develop from branched molecules by intramolecular reactions.

Figure III-2 Schematic time-temperature-transformation state diagrams for the curing process.

(a) A thermosetting system not involving phase separation.

(b) A thermosetting system in which a rubber phase may separate during cure. (T_s is the maximum temperature for the phase separation to occur prior to gelation.)

(Note: Vitrification above $T_{g\infty}$ can occur as a consequence of degradation only in some systems.)



and, after cure, the thermomechanical behavior with the same specimen. Times to gelation and to vitrification are measured by the lapsed times to the maxima of the dynamic mechanical loss peaks; transition temperatures are similarly located with respect to temperature.

A Generalized Time/Temperature/Transformation State Diagram for Thermosetting Systems

Figure III-2a and its ramifications form the basis of the following discussion. For a thermosetting system involving separation of a discrete rubber phase the diagram is modified to include a phase separation line (e.g., a cloud point locus) as in Figure III-2b which is alluded to later.

Consideration of the cure of a liquid thermosetting system at a series of constant temperatures (Figure III-2)(Gillham, 1980, 1981b) leads to the conclusion that there will be three main types of behavior, depending on the temperature of cure (Babayevsky and Gillham, 1973).

At elevated isothermal temperatures, above the maximum glass transition temperature of the cured system $T_{g\infty}$, a curing liquid gels and forms an elastomer (rubber), but does not vitrify in the absence of degradation. (Figure III-2 actually includes an effect of degradation above $T_{g\infty}$--see caption and later text.)

At intermediate temperatures (${}_{gel}T_g < T_{cure} < T_{g\infty}$), the curing liquid first gels and later vitrifies. ${}_{gel}T_g$ is the isothermal temperature at which gelation and vitrification occur simultaneously.

At low temperatures, above the glass transition temperature of the reactants ${}_{resin}T_g$ but below ${}_{gel}T_g$, the viscous curing liquid can vitrify before reaching the chemical conversion necessary for gelation to occur simply by an increase of molecular weight. If chemical reactions are quenched by vitrification, after vitrifying the material need not gel.

The time to gelation is expected to decrease exponentially with increasing temperature because, according to gelation theory (Flory, 1953), the chemical conversion at gelation is constant. Activation energies for the reactions leading to gelation can therefore be obtained from plots of the logarithm of the time to gelation versus reciprocal absolute temperature (Babayevsky and Gillham, 1973; Gillham, 1979; Gillham et al., 1974; Schneider et al., 1979, 1980).

The time to vitrification passes through a minimum between ${}_{gel}T_g$ and $T_{g\infty}$ (Gillham et al., 1974). This reflects the competition between the increased rate constants for reaction and the increasing chemical conversion required for vitrification at higher temperatures.

The maximum in the time to vitrify below ${}_{gel}T_g$ arises because of the competition between the temperature- and time-dependences of viscosity of the reacting system (Gillham, 1981a).

It is apparent that if reactions are quenched by the process of vitrification ($T_{cure} < T_{g\infty}$), the glass transition temperature (T_g) of the system after isothermal cure will then equal T_{cure}. The vitrification curve then provides the minimum time to reach the glass transition temperature that the reactive system can attain at temperature T_{cure}. It also follows that ${}_{gel}T_g$ is the glass transition temperature of the reactive system at its point of gelation (Babayevsky and Gillham, 1973).

The cure-state diagram therefore shows that the thermosetting process is usefully characterized by the three temperatures ${}_{resin}T_g$, ${}_{gel}T_g$ and $T_{g\infty}$, which will vary from system to system (Gillham, 1979).

The temperature between ${}_{gel}T_g$ and $T_{g\infty}$ at which the time to vitrification is a minimum may be of practical importance beyond being the most economical temperature for producing solid from fluid. As a consequence of the exothermic reactions, cure of specimens below this temperature will lead to the inside vitrifying before the outside, whereas cure at higher temperatures will lead to the outside vitrifying before the inside. The volumetric shrinkage on vitrification will result in a skin/core structure for the latter case with built-in curing stresses. (This type of structure also occurs when materials are cooled externally after cure because the outside cools more rapidly than the inside.)

Whereas ${}_{resin}T_g$, ${}_{gel}T_g$, and $T_{g\infty}$ are singular physical transition temperatures definable by a temperature (and time scale), thermal degradation cannot be so easily defined. Thermal degradation can lead to a gelled glass (as in Figure III-2); however, other types of degradation can lead to other physical states (e.g., ungelled glass, liquid, and gas).

The cure-state diagram explains a number of practices in the field of thermosets. If the storage temperature is below ${}_{gel}T_g$, a reactive fluid material will become a vitrified solid of low molecular weight. This solid will be stable and can later be liquefied by heat and processed. At temperatures above ${}_{gel}T_g$, the stored material will have a finite shelf life for subsequent processing because gelation will occur before vitrification. (A gelled material does not flow in the usual sense.) This concept is the basis of a widespread empirical technology that includes thermosetting molding compounds and prepregs with latent reactivity.

In general, and in principle, if $T_{cure} < T_{g\infty}$, a reactive material will vitrify and full chemical conversion will be prevented; the material then usually will need to be postcured above $T_{g\infty}$ for development of optimum properties. For the manufacture of objects of finite size, it is necessary to go through a multistep process because of the exothermic nature of the reactions. A more sophisticated approach for controlling highly exothermic systems using vitrification is to cure the material by raising the temperature at a rate such that T_g and T_{cure} coincide (Gillham, 1979). For highly cross-linkable or rigid-chain polymeric materials, $T_{g\infty}$ can be above the limits of thermal stability, in which case full chemical conversion of the original network-forming reactions usually would not be attainable. Such incompletely reacted systems should be susceptible to complications on aging. In general then systems should be designed such that $T_{g\infty}$ is attainable. Further, for composite materials in which a component other than the cured resin is thermally sensitive, $T_{g\infty}$ for the thermosetting resin should be below temperatures that would lead to damage of any part. (An example would be adhesive bonding of certain alloys of aluminum by a thermally stable epoxy.) Similarly, if a composite system cannot be heated above a limiting temperature for some practical reason (e.g., size), then the curing system should have its $T_{g\infty}$ below that limiting temperature. (An example would be painting an airplane in a hangar.)

It should be feasible to design systems molecularly such that $T_{g\infty}$ is above T_{cure}. Suggestions for reactions in the glassy state include cure by small molecules able to diffuse through the glassy state (as in chain reactions), incorporation of sterically well-situated latently reactive groups in the polymerizing system, and employment of systems with prominent glassy state relaxations.

The extent of cure affects not only the value of the glass transition but also properties at temperatures well below it. For example, the modulus at room temperature can be decreased and the intensity of the $T < T_g$ relaxations (as measured by the area under dynamic mechanical loss peaks) can be increased by postcure (Gillham, 1979; Lewis et al., 1979). This suggests that the free volume in the glassy state is increased and that the density at room temperature is decreased as consequences of the postcure in spite of the increase of T_g (Doyle et al., 1980, Gillham, 1981b). This is presumably a result of the glassy state being further from equilibrium at room temperature the higher the T_g. Subsequent spontaneous physical aging at room temperature leads to densification and embrittlement. The increased free volume on cooling after postcure at higher temperatures has been held responsible for the increase in water absorption of epoxies on immersion (Doyle et al., 1980).

If $T_{g\infty}$ is below room temperature, the polymer system will be used as an elastomer.

The cure-state diagram of Figure III-2 is idealized in several respects.

If there are competing network-forming reactions having different reaction rates, then different temperature/time paths will lead to different molecular networks in the fully cured materials and to different material behavior. $T_{g\infty}$ and ${}_{gel}T_g$ will vary accordingly. For example, values for $T_{g\infty}$ may be higher after prolonged initial cure at lower temperatures prior to post-cure at higher temperatures (Lewis et al., 1979; Schneider and Gillham, 1980).

Vitrification times will be longer than those measured operationally to the time of the peak of the dynamic mechanical loss maximum assigned to the vitrification process because vitrification, with respect to the quenching of reactions, is more properly defined when the rigidity levels off (Gillham, 1979; Schneider and Gillham, 1980).

The macroscopic assignment of gelation by an isoviscous measurement does not necessarily correspond to its molecular definition, which corresponds to an isocompositional state. However, values obtained rheologically for the activation energies of reactions leading to gelation can approximate those determined from times to attain a fixed chemical conversion (Gillham, 1979; Schneider et al., 1979).

The state diagram of Figure III-2 has been obtained experimentally from a series of isothermal reactions. A similar diagram can be obtained for a given system from a series of temperature-programmed scans from low to high temperature at different heating rates (Enns et al., 1980; Lewis et al., 1979). A typical scan will then successively reveal: glassy-state relaxations of the untreated resin below its glass transition, resin T_g, gelation, vitrification, the glass transition of the incompletely cured material, and above $T_{g\infty}$ revitrification caused by degradation.

Extension to Phase Separation During Cure in Rubber-Modified Systems

The cure-state diagram of Figure III-2b is a schematic time/temperature/transformation state diagram including the onset of phase separation in two-phase systems. (Rubber is often incorporated in inherently brittle polymeric materials as a method for increasing toughness. The curing of rubber-modified systems often involves change from an initially homogeneous solution to a heterogeneous multiphase morphology.) Evidence has been presented to show that the process of gelation arrests the development of morphology, and, therefore, that the time to gelation can be used to control material properties (Gillham et al., 1977). Gelation time can be varied by catalysts. Similarly, by reaction at different temperatures, a single chemical composition can produce distinctly different morphologies. The temperature of gelation is, therefore, a characteristic one for defining the morphology developed isothermally by a particular system (Manzione et al., 1981a).

Rubber particles nucleate and grow during the polymerization process. In general, as in crystallization of linear polymers, nucleation is favored by low temperatures (being limited by the glass transition of the material), whereas growth is favored by high temperatures. The overall extent of phase separation can, therefore, be expected to be at a maximum at intermediate temperatures (Manzione et al., 1981b).

Quenching of the development of morphological changes by the phenomenon of gelation may be explained by an abrupt decrease in diffusion of rubbery material to the growing domains of rubber that occurs in the transformation from a viscous liquid to a soft gel, as large molecules form in the process of gelation. This is a longer range and larger scale diffusion process than that involved in the quenching of chemical reactions that occurs in the transformation from a rubbery or liquid state to a glassy state (vitrification) by restrictions on the more localized motions of chemically reactive parts of the molecules.

Extension to Linear Systems (e.g., Polyimides)

Polyimides generally have been applied as solutions of polyamic acids (the reaction product of a dianhydride and diamine) that are then polymerized in situ to the polyimide stage (by ring-closing of the polyamic acid). They resemble, therefore, thermosetting systems in that their chemistry and processing are intertwined in a process that can again be called cure. If the maximum glass transition temperature $T_{g\infty}$ of the polyimide is above the maximum temperature of reaction, then vitrification will occur, leading to quenching of chemical conversion and a T_g reflecting the polymerization conditions rather than the structure of the desired polyimide (Gillham and Gillham, 1973). As with network-forming systems, this will interfere with attempts to relate properties to structure.

Gelation, in Flory's molecular sense, does not occur with linear systems and so would not be expected in linear systems. However, because the macroscopic measurement of gelation corresponds to the attainment of an isoviscous state, the attainment of that isoviscous state may well be in itself a measure of limits to diffusional processes (such as flow and phase separation). The time/temperature/transformation state diagram (Figure III-2) and its consequences may therefore be directly applicable to linear systems such as polyimides.

CHARACTERIZATION

For a given cured neat resin (with no inclusions) innumerable characterization techniques are available to provide numerical values of bulk mechanical properties and of parameters that affect mechanical behavior. (The dependence of mechanical properties on test frequency, temperature, and aging time is an essential part of characterization.) In principle these data are immediately useful for the design of composite materials; however, it should be noted that many standardized tests provide data that cannot be extrapolated to geometries and sizes other than those used in the test. Only with caution are they useful for comparing materials.

Further, because of the numerous formulations of uncured resin and the different states of cure and aging, most specimens are unique, and the data are useful only in general terms for very similar systems. The user of a given system is likely to evaluate extensively only the composite, not only because of its immediate utility but also because of difficulties in relating results of tests on neat and composite systems. Characterization of neat cured castings and neat moldings should serve as a basis for predicting properties of composites. It is useful for examining important complications of the matrix per se.

The previous sections emphasized relationships between the cured state and the process of cure. It is implicit that characterization of the cured state also relates directly to the process of cure. The principal approaches for characterization of neat matrix materials are summarized in general terms in the following paragraphs.

1. Nondestructive methods can provide the first level of information. In addition to dynamic mechanical and other low-strain mechanical tests, characterization data that bear on material behavior include T_g, secondary relaxations ($T < T_g$), cross-link density, solubility parameter, and dielectric properties. Two-phase rubber-modified systems designed for toughness lend themselves to morphological studies using optical and electron microscopes. A controversy exists concerning the morphology of neat epoxy systems (Dušek et al., 1978; Mijovic and Koutsky, 1979). The techniques of thermal analysis, including differential scanning calorimetry and thermogravimetric analysis, provide a methodology for investigation of physical and chemical changes, including degradation, versus temperature. These characteristics should be useful in providing the upper temperature for structural use (T_g) and thermal stability, and for providing the temperatures and frequencies at which properties of the solid material change (secondary relaxations).

2. Destructive methods (e.g., tensile, compressive, and shear stress-strain to yield and to break at low- and high-strain rates; and fracture-toughness and fatigue experiments), in principle provide engineering data (modulus, Poisson's ratio, yield, ultimate strength and elongation, fracture-energy toughness, and lifetime under cyclic loads). This is a crucial area because the matrix is typically the weak link when stress is applied transverse to the filaments of the composite.

3. Spectroscopic techniques are molecular probes. All are becoming more powerful under continuous development. Techniques include IR spectroscopy (Fourier transform), Raman spectroscopy, nuclear magnetic resonance, electron spectroscopy (ESCA), and fluorescence. Together they provide a basis for elucidating molecular architecture and dynamics, and for monitoring subtle changes that eventually lead to failure (e.g., bond rupture in aging).

4. Pyrolysis-effluent gas analysis permits study of stability to heat.

5. Several techniques are used for characterizing cure. Gelation and vitrification times can be measured in one experiment by dynamic mechanical methods using supported specimens (e.g., coated substrates). The fractions of soluble and insoluble material can be measured directly,

as can shrinkage, during cure. Changes in viscosity to gelation can be measured by standard rheological methods. Calorimetric methods monitor the kinetics of chemical conversion during cure by the heat evolved on polymerization. The spectroscopic techniques, especially Fourier transform IR, monitor the disappearance or appearance of specific molecular groupings. Thermosetting materials are difficult to characterize: the limitations reside as much in the systems themselves as in the techniques. The gross approach taken in their empirical development and manufacture has led to average systems that are forgiving with respect to purity of reactants, conversion during cure, and treatment after cure. Intense scientific investigation will surely lead to criteria and subtleties that will be exploited for the purpose of producing better materials.

CONCLUSIONS

1. Thermoset polymers are being used successfully as matrices in high-technology composite material systems. Commercial applications of these composites are growing rapidly.

2. Thermosetting matrix materials have been developed largely empirically. The industry uses proprietary formulations of relatively impure chemicals in empirical cure cycles. There is a tendency to use a limited number of rather arbitrary formulations.

3. The polymer science of thermosetting (mostly network molecule) materials has been neglected in comparison with that of thermoplastic (linear molecule) materials. The reason lies in the stringent conditions required for linear versus network polymerization reactions. Unlike thermoplastics technology, thermoset technology was able to advance without a mature polymer science.

4. Powerful capabilities for research have arisen recently as a result of the advent of new separation techniques (e.g., preparative liquid chromatography for monomers and oligomers) and advanced analytical techniques (e.g., Fourier transform IR). Investigation of model systems will result in a better understanding of the influence of chemistry on thermosetting material properties.

5. An intellectual framework exists in the form of a temperature/time/transformation state diagram for understanding the relationships of the process of cure to the properties of the cured state.

6. Use of model systems cured appropriately will facilitate the investigation of the physics of the glassy state for the ultimate objective of designing and making improved systems and of removing potential problems in current systems.

7. The scientific basis of ultimate behavior (fracture, fatigue, and aging) is not well developed.

8. The scientific basis of fiber and matrix interactions is not well developed.

RECOMMENDATIONS

1. Because of the newly available separation and analytical techniques, basic research on thermosetting matrix systems should use model systems.

2. Molecular structure and macroscopic property relationships should be the theme for developing the polymer science of thermosetting matrix materials. Numerous powerful nondestructive techniques are available and should be applied for this purpose.

3. Relationships between the process of cure and properties of the cured state should be investigated.

4. Fracture-initiating processes and toughening mechanisms should be investigated.

5. Time effects caused by physical (including fatigue) and chemical aging should be investigated, and accelerated testing methods should be developed.

6. The effects of water vapor and other physical and chemical environments should be investigated.

7. Fiber and polymer interactive phenomena should be isolated.

8. A set of desirable matrix properties should be defined for predicting in conjunction with fiber properties, the properties of the composites.

9. Tests on unfilled matrix material should be designed that translate directly to useful data on the composite.

REFERENCES

Babayevsky, P. G., and J. K. Gillham, "Epoxy Thermosetting Systems: Dynamic Mechanical Analysis of the Reactions of Aromatic Diamines with the Diglycidyl Ether of Bisphenol A," *J. Appl. Polym. Sci.*, *17*, 2067-2088 (1973).

Doyle, M. J., J. K. Gillham, S. J. Washburn, and C. A. McPherson, "Structure/Property Relationships of High Temperature Epoxy Resins," *Amer.. Chem. Soc. Div. Org. Coatings Plast. Chem. Prepr.*, *43*, 677-679 (1980).

Dušek, K., J. Pleštil, F. Lednicky, and S. Luňák, "Are Cured Epoxy Resins Inhomogenous?," *Polymer*, *19*(4), 393-397 (1978).
Enns, J. B., J. K. Gillham, and M. J. Doyle, "Investigation of the Cure of Thermosetting Epoxies by an Automated Torsion Pendulum," *Amer. Chem. Soc. Div. Org. Coatings Plast. Chem. Prepr.*, *43*, 669-676 (1980).

Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., 1953.

Gillham, J. K., "A Semimicro Thermomechanical Technique for Characterizing Polymeric Materials: Torsional Braid Analysis," *Amer. Inst. Chem. Eng. J.*, *20*(6), 1066-1079 (1974).

Gillham, J. K., "Formation and Properties of Network Polymeric Systems," *Polym. Eng. Sci.*, *19*(10), 676-682 (1979).

Gillham, J. K., "A Generalized Time-Temperature-Transformation Phase Diagram for Thermosetting Systems," *Soc. Plas. Eng.*, *Annual Tech. Conf.*, New York, *Proceedings*, pp. 268-271 (1980).

Gillham, J. K., "Torsional Braid Analysis (TBA) of Polymers," in *Developments in Polymer Characterization - 3*, J. V. Dawkins, ed., Applied Science Publishers, U.K. (1981a)

Gillham, J. K., "The Time-Temperature-Transformation (TTT) State Diagram and its Role in Determining Structure/Property Relationships in Thermosetting Systems," *Amer. Chem. Soc. Div. Org. Coatings Plast. Chem. Prepr.*, *44*, 185-191 (1981b).

Gillham, J. K., J. A. Benci, and A. Noshay, "Isothermal Transitions of a Thermosetting System," *J. Polym. Sci.*, Symposium No. 46, 1974, pp. 279-289.

Gillham, J. K., and H. C. Gillham, "Polyimides: Effect of Molecular Structure and Cure on Thermomechanical Behavior," *Polym. Eng. Sci.*, *13*(6), 447-454 (1973).

Gillham, J. K., C. A. Glandt, and C. A. McPherson, "Characterization of Thermosetting Epoxy Systems Using a Torsional Pendulum," *Chemistry and Properties of Crosslinked Polymers*, S. Labana, ed., Academic Press, Inc., New York, 1977, pp. 491-520.

Lewis, A. F., M. J. Doyle, and J. K. Gillham, "Effect of Cure History on Dynamic Mechanical Properties of an Epoxy System," *Polym. Eng. Sci.*, *19*(10), 683-686, (1979).

Manzione, L. T., J. K. Gillham, and C. A. McPherson, "Rubber-Modified Epoxies: Transitions and Morphology," *J. Appl. Polym. Sci.*, *26*, 889 (1981a).

Manzione, L. T., J. K. Gillham, and C. A. McPherson, "Rubber-Modified Epoxies: Morphology and Mechanical Properties," *J. Appl. Poly. Sci.*, *26*, 907 (1981b).

Mijovic, J. S., and J. A. Koutsky, "The Effect of Postcure Time on the Fracture Properties and Nodular Morphology of an Epoxy Resin," *J. Appl. Polym. Sci.*, *23*(4), 1037-1042 (1979).

Morgan, R. J., and J. F. O'Neal, "The Durability of Epoxies," *Polym-Plast. Tech. Eng.*, *10*(1), 49-116 (1978).

Ophir, Z. H., J. A. Emerson, and G. L. Wilkes, "Sub-Tg Annealing Studies of Rubber-Modified and Unmodified Epoxy Systems," *J. Appl. Phys.*, *49*(10), 5032-5038 (1978).

Riew, C. K., E. H. Rowe, and A. R. Siebert, *Toughness and Brittleness of Plastics*, R. D. Deanin and A. M. Crugnola, eds., American Chemical Society, Washington, D.C., 1976, Chapter 27.

Schneider, N. S., J. F. Sprouse, G. L. Hagnauer, and J. K. Gillham, "DSC and TBA Studies of the Curing Behavior of Two Dicy-Containing Epoxy Resins," *Polym. Eng. Sci.*, *19*(4), 304-312 (1979).

Schneider, N. S., and J. K. Gillham, "TBA Studies of Prepreg Curing Behavior," *Polym. Composites*, *1*(2), 97-102 (1980).

Struick, L. C. E., *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier Publishing Co., Amsterdam, 1978.

CHAPTER IV

FABRICATION OF COMPOSITE COMPONENTS

The fabrication technology for advanced composites has developed in an empirical fashion as an extension of the experience with fiberglass. Most of the thrust for this technology came from applications to military aircraft (wing structures, empennage, fuselage, fittings, helicopter structures, and engine structures). An extensive literature exists in the form of government reports, that deals with the fabrication of various specific components and structures. More generalized manufacturing processes have been discussed in a military handbook (DOD, 1971) and in reports by Grumman (1970), Northrop (1971), and Lockheed-Georgia (1975). Detailed overviews of fabrication of composites are given in the Advanced Composites Fabrication Guide (Lockheed-Georgia, 1976), the Advanced Composites Design Guide (Rockwell International, 1977), and by Borstell (1980). Current applications, in addition to military aircraft, include civil aircraft (control surfaces and floor columns), space structures, automotive and boat components, biomedical engineering products, and leisure products. A general overview of the science base for composites processing was given by Noton (1979) in an NMAB report.

The manufacturing process is one of the most important stages in assuring that the finished component meets design specifications. The process involves specification of the basic components (i.e., fiber and matrix), and their combination (i.e., material system, selection of a fabrication method, and the requisite tooling and equipment), cost analysis, and quality assurance. The objective is to produce a high-quality component that meets specifications at a minimum cost.

Initially, the primary requirement in design and fabrication of composite structures was weight savings. Later, cost competitiveness with more conventional procedures became equally important. To these two requirements today is added the need for assurance of quality, reproducibility, and predictability of behavior over the lifetime of the structure.

The quality of fabricated composite articles is highly dependent on the manufacturing standards adopted and enforced during the fabrication process. Quality control standards must be applied at all phases of fabrication: inspection of incoming prepreg, lay-up or other procedures, preparation for curing, curing cycle, and subsequent machining, bonding, or joining operations. Constant monitoring must be maintained during all these phases to insure compliance with detailed process specifications.

This chapter presents a brief review of the state of the art of various fabrication processes followed in the conversion of a fiber and matrix into a composite structural component, integrally molded assembly, or cocured sandwich structure. Secondary operations are also discussed, such as machining of cured laminates and joining of parts by adhesive bonding or mechanical fastening. The advantages and limitations of the various processes and the area of needed improvement are discussed.

MATERIALS

The starting materials and the basic components were discussed in detail in the preceding chapters. Advanced composites are produced by combining high-performance fibers with a suitable matrix. The fibers usually control the longitudinal strength and stiffness, formability, and machinability of the laminate. The matrix determines the transverse strength and stiffness, intralaminar (in-plane) and interlaminar shear strength, service temperature, and laminating process. Proper processing, including control of fiber orientations, fiber volume ratio, and subsequent machining and bonding operations, insures that the product meets the desired specifications, such as light weight, high fatigue endurance, and low cost.

Fibers

The most commonly used fibers are glass, graphite, aramid, and boron. Glass fibers used are typically of Eand S-glass with moduli of 72.5 GPa (10.5 x 10^6 psi) and 85.6 GPa (12.4 x 10^6 psi), respectively. Their strengths also vary accordingly, 3.450 GPa (5.00 x 10^5 psi) and 4.485 GPa (6.50 x 10^5 psi) for Eand S-glass, respectively.

Graphite fibers can be classified into four basic types by modulus. The low-cost, high-strength fibers are common in aircraft structures. The most common among these are Thornel-300 (T300) and AS types. These have moduli of 207 to 235 GPa (30 to 34 x 10^6 psi) and strengths of 2.070 to 2.898 GPa (3.00 to 4.20 x 10^5 psi). The high-modulus fibers are used in engine and spacecraft applications. The use of intermediate or ultra-high modulus fibers has been limited.

Aramid (or Kevlar or PRD-49) is an organic fiber developed by DuPont, with a modulus of 131 GPa (19 x 10^6 psi). It has high strength, very low density, high elongation, and potentially low cost.

Boron filaments were the first advanced fibers introduced after the glass fibers. They have high moduli ranging from 345 to 414 GPa (50 to 60 x 10^6 psi) and high strength ranging from 2.760 to 3.519 GPa (4.00 to 5.10 x 10^5 psi). They have relatively large diameters ranging between 0.051 and 0.203 mm (0.002 and 0.008 in.). Boron filaments are hard and brittle and are difficult to bend into radii smaller than 2.54 cm (1 in.). In some design applications, mixtures of these fibers are used to obtain a balance of properties not possible with a single fiber.

The most common hybrid composites employ mixtures of graphite and glass fibers to reduce costs of lightly loaded structures and graphite with aramid plies on the outside for increased impact damage tolerance.

Matrices

The most highly developed organic matrices are the epoxies. Two epoxy systems are commonly used: (1) 121°C (250°F) systems for helicopter and sporting goods applications, and (2) 177°C (350°F) systems for applications to jet transports, military aircraft, and space structures. The first system requires shorter cure cycles, resulting in cost savings during production. The second system is usually cured for 1 hour at 176°C (350°F) under 345- to 690-kPa (50- to 100-psi) pressure. Parts made of this system can be designed to operate at 176°C (350°F) under dry conditions and at 132°C (270°F) under wet conditions. Polyimide matrices are applicable to jet engine parts and structures exposed to higher temperatures. There are two types of polyimide resins used in composites, primarily with graphite fibers: (1) condensation type, which has the best thermal stability (315°C to 371°C; 600°F to 700°F), and (2) addition type, which is easier to process, but is used for somewhat lower temperature applications (232°C to 288°C; 450°F to 550°F). Thermoplastics, which are compatible with hot forming and injection molding, are finding increasing applications in lightly loaded structures encountered in the automobile industry. Molding costs are appreciably reduced because parts can be made in 10 to 15 minutes under pressure at a temperature slightly above the resin-softening temperature. Thermoplastic resins suitable for composite structures include polysulfone, polycarbonate, poly(ether sulfone), poly(ethylene sulfide), nylon, and polypropylene. One of the most commonly used resins for quick-curing systems in commercial applications is polyester. It is also preferred in automotive applications, especially with chopped glass fibers.

Material Forms

Fibers are preimpregnated with resin by the prepreg manufacturers and are supplied to the composite fabricator or user in a variety of forms. The manufacturers respond to a set of procurement specifications such as fiber volume ratio, ply thickness, and degree of B-staging (drape). The prepreg manufacturers modify or develop resin systems, purchase fibers, combine fibers and resin into usable forms, test samples as required, and certify that their product conforms to specifications.

The various prepregs are available in the form of tape or cloth. Boron prepregs come in the form of 7.62- to 15.24-cm (3- to 6-in.) wide tape. Graphite prepregs are available in the forms of 7.6- to 122-cm (3- to 48-in.) wide tape and 30- to 122-cm (12- to 48-in.) wide cloth. Kevlar is also available in the form of tape and cloth. Prepreg preparation is illustrated in Figure IV-1. It includes the following stages: fiber control, collimation, impregnation with resin, and tape production.

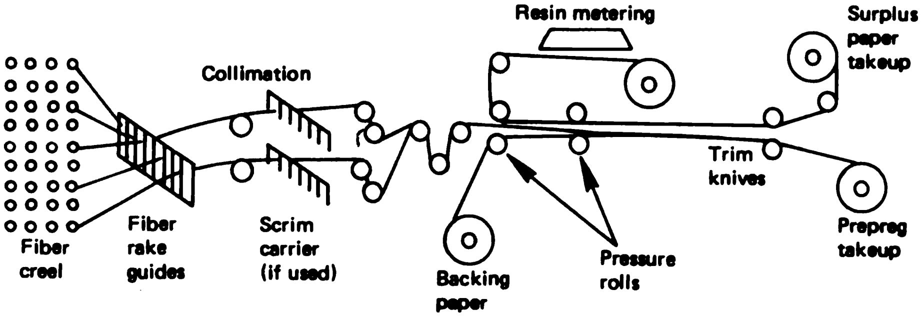


Figure IV-1. Warm pressing of fibers into B-stage resin film.

Support Materials

Laminating of advanced composite materials requires the use of several expendable support materials such as peel ply, bleeder cloth, separator, breather plies, bagging, bag seal, and mold release materials. Bleeder plies are normally glass cloth layers used to remove all excess resin during cure. Breather plies are also dry glass cloth layers. Separator and sealer plies are normally Teflon-impregnated glass cloth.

Prepreg Storage

Composite prepreg tapes are obtained in a partially cured state, the so-called B-stage. The curing process is a temperature and time reaction in which the time and temperature required for complete cure are inversely related. Thus, the prepreg can be cured at any given temperature if sufficient time is allowed. This implies that the shelf life of the B-staged prepreg is limited. In general, it is assumed conservatively that most prepregs have a shelf life of 3 months at a storage temperature of -18°C (0°F). It has been shown, however, that the quality of the cured laminate does not deteriorate much even after storage periods of up to 2 years in the freezer. The only drawback noticed in such cases is some difficulty in handling.

To insure uniformity of quality and reproducibility, recommended procedures for storage and handling of epoxy prepregs should be followed (Lockheed-Georgia, 1976). Overaging should be avoided by careful inventory control. A complete record should be kept of the times the prepreg is out of the refrigerator and exposed to ambient temperatures. The total time out of refrigeration is limited to 10 days. To avoid any moisture absorption by the prepreg, all packages removed from storage should be allowed to reach room temperature before the plastic container is unsealed.

FABRICATION METHODS

The goals of the fabrication process are to control the fiber orientation and location, ply thickness, fiber volume ratio, and to minimize voids and residual stresses. The choice of a manufacturing process depends on many factors, such as size and geometry of the part, functional and appearance requirements, type of composite material, production volume and rate, availability of facilities, weight, cost, and durability.

Many of the processing techniques and equipment used in manufacturing fiberglass-reinforced plastic parts are applicable to boron, graphite, carbon, Kevlar, and other high-strength and high-modulus fibers. Slight variations in such areas as material handling, cutting, shaping are usually anticipated, depending on the type of reinforcement used in the composite.

The fabrication process consists of the following steps:

1. Layup,
2. Preparation for cure,
3. Cure, and
4. Machining and joining.

The most common methods are discussed in the following paragraphs.

Autoclave Molding

This method is the most commonly used in industry today. It is tailored to the low-volume production runs typical of aerospace needs. It is used to fabricate a variety of aerospace components, including those of complex shapes, double contours, and large dimensions. The process consists of cutting the prepreg to shape, laying up the blanks in the mold, preparing a bleeder system, bagging, and curing.

Lay-up

First the prepreg is cut in the desired shape with the desired fiber orientation. This is done either manually or mechanically. Large aerospace companies use automated cutting equipment with laser beams or water jets and employ computer controls. Improved material-handling techniques are being incorporated for the transfer of the composite plies to the lamination area.

Two modes of lay-up are used: "ply-on-ply": and "ply-on-film." The former is a single-step process limited to simple contours and ply shapes. The various plies are laid on top of each other directly onto the mold surface (Figure IV-2). In this case, inspection of the lay-up is difficult and repairs necessitated by defective material and improper machine operation are time consuming and may delay the production schedule. The ply-on-film mode consists of laying the various plies on individual plastic (Mylar) templates and then transfering them and stacking them on the tool (Figure IV-3). This is a more universal method that does not suffer from the disadvantages of the ply-on-ply method. However, the transfer and stacking operations increase the requirements for labor and facilities and add the cost of the template film. Both of these lay-up methods are being used in current production, and they have both been automated.

One approach for more automated processing of tapes is to purchase alternative material forms made on automated facilities at the material supplier's plant. This procedure reduces handling in the fabricator's facility. Alternative forms include tapes up to 122 cm (48 in.) in width, unidirectional, cross-ply sheets, fabrics, and quasi-isotropic sheets ready to be cut and laid up onto the tool. Automated lay-up machines are used now to convert prepreg into fully laid-up parts. The systems include prepreg trimming units, robotic or flip-table stacking units, and TV cameras for lay-up inspection. These automated systems are essential for cost-effective large-scale production.

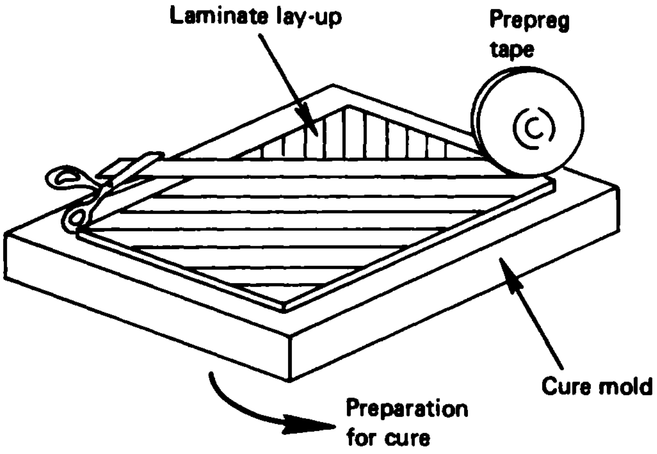


Figure IV-2. Ply-on-ply laminate lay-up method (Lockheed-Georgia, 1976).

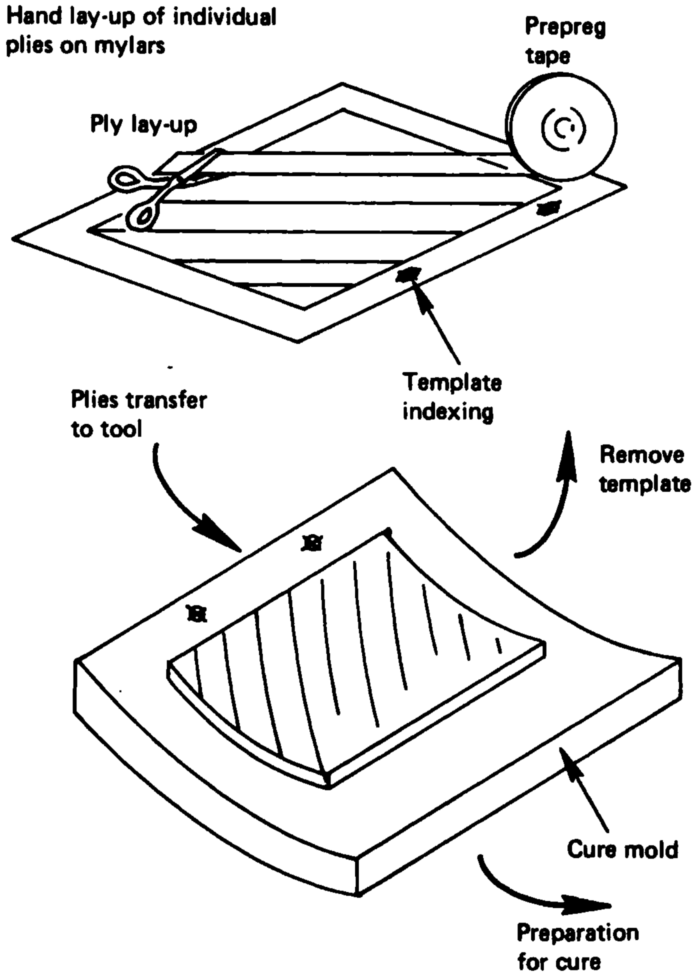


Figure IV-3. Ply-on-film laminate lay-up method (Lockheed-Georgia, 1976).

Following the lay-up, prepreg trimming and cutting may be necessary. Manual trimming is a slow process and subject to human error. Numerically controlled techniques employing lasers, water jets, or reciprocating knives are now being used.

Bleeder/Breather System

To maintain the specified fiber volume ratio, a controlled-capacity bleeder/breather system is prepared to absorb excess resin and to permit the escape of volatiles. Bleedout may be through the edges of the laminate (edge bleedout), through the top surface (vertical bleedout), or a combination of both. Bleeder and breather materials are typically glass cloth or mat. The bleeder-to-prepreg ratio for a given prepreg is given by the prepreg supplier. In cases of thick parts with many partial plies, wrinkling may occur unless the lay-up is compacted (debulked) periodically. This is done by heating the lay-up with one bleeder layer in place under vacuum. For graphite epoxy this is done for every 10 to 20 plies. To minimize or eliminate the need for bleeding during the final cure, prebleeding is done under vacuum at a lower temperature, typically 82°- to 107°C (180°- to 225°F). Uniform bleedout of thick parts, especially parts of varying thicknesss, is difficult. Nonuniform bleedout results in variations of fiber volume ratio and residual stresses within the laminate and may cause distortions and warpage of even symmetric laminates. In some recent applications, special prebled prepreg that does not require bleeding during cure has been used. No quantitative evaluation exists of the products produced by this process.

Vacuum Bagging

The lay-up with the bleeder/breather system is enclosed in a vacuum bag for drawing of vaccuum during cure. This is a critical step for the quality of the part. The vacuum bags are usually made of nylon or polyimide film and sealed with a sealant. They are usually disposable and have the disadvantages of material costs, labor costs, and risk of defects. For large-scale production, contoured, reusable silicone rubber bags are recommended. One type of reusable bag developed consists of fabric-reinforced silicone rubber. Such bags have withstood 800 autoclave bonding cycles with minimal maintenance. However, such bags made by brush impregnation of silicone resin and solvent often do not meet Occupational Safety and Health Administration regulations. Suggestions have been made for developing a coating that can be sprayed over the lay-up and bleeder assembly to form an air-tight, thermally stable, extensible bag, as well as for developing high-elongation films that can be stretched over the assembly and seat snugly with vacuum (Noton, 1979). The current trend to reduce the peak curing temperature of 177°C (350°F) should make it easier to use less expensive organic rubber compounds as bagging material. The vacuum bag becomes effective only if it is sealed tightly and if a high-capacity vacuum path to the composite lay-up is provided.

Curing

The bagged mold is transferred to an autoclave for curing of full vaccuum and is subjected to a pressure, temperature, and time cycle. Processing of boron-reinforced epoxy and Kevlar-reinforced epoxy has been fairly well standardized. However, autoclave curing of graphite reinforced epoxy with 177°C (350°F) curing epoxy is more complex, as it is more difficult to deaerate these materials. Initially, the lay-up is heated at a rate of 2 to 4°C (3 to 7°F) per minute under full vacuum to melt the resin and remove the volatiles. At a specified temperature, usually between 107°C and 127°C (225°F and 260°F), a pressure of approximately 550 to 690 kPa (80 to 100 psi) is applied and maintained. This temperature is selected to maintain the resin viscosity at a high enough level to allow volatile removal without excessive bleeding. Thirty to sixty minutes later, the vacuum is reduced or dropped, and the temperature is increased to the peak curing temperature at rate of 2 to 4°C (3 to 7°F) per minute. The part is held at this temperature for 1 to 2 hours.

The cool-down step is sometimes controlled to prevent microcracking caused by residual stresses. It has been shown theoretically that the residual stresses introduced during curing depend on the specific cool-down path (Weitsman, 1979). More investigation, theoretical and experimental, is needed to optimize the cool-down path with regard to residual stresses. Postcuring off the tool in an unrestrained position is sometimes recommended to achieve the best properties for the part.

Polyimide matrix composites require cure schedules that vary with the type of polyimide used. These cure cycles have not been standardized yet.

Process Limitations and Research Needs

Although autoclave molding has been employed for many years, it has several limitations. The process is fairly slow and labor intensive, and the quality of the product is highly dependent on the experience and skill of the labor force. The use of broad goods, prelaid composite sheets, and the introduction of automatic prepreg cutting and tape-laying machines is alleviating this problem.

Manual operations during the lay-up process make quality inspection more critical. Careful supervision and inspection are necessary to avoid entrapment of air or foreign matter, ply gaps, ply overlaps, and ply misalignment. Current quality control methods are not standardized, leading to either excessive wastage or extensive qualification testing. More standardization and automation in the lay-up and inspection stages would alleviate the problem.

Bagging and sealing operations for autoclave cure could be improved by the introduction of reusable or sprayable bags and the careful provision for effective vacuum path.

There are no well-established curing cycles for the various prepregs. Thick parts, especially those of varying thickness, present problems because of thermal and gel gradients through the thickness. There is need for on-line monitoring of degree of curing, using dielectric probes or other sensors, with automatic feedback process control. The heat transfer phenomenon from the surrounding medium of the autoclave through the vacuum bag on one side and the tool on the other should be studied. On-line monitoring of volatiles and outgassing during cure should be correlated with chemical and mechanical changes. Methods should be developed for optimum pressure and temperature and time profiles, including control of residual stresses. Whenever possible and tolerable, techniques for rapid curing should be investigated, especially for products produced in large volume.

Vacuum Bag Molding

This type of molding is similar to autoclave molding except that no external pressure is applied to the bagged lay-up. It does not produce parts as dense as those produced by autoclave molding; however, it is an adequate process for components that are not heavily loaded.

Compression Molding

Matched-die molding techniques are extensions of the autoclave molding process. These molding processes are aimed at large-volume components for which the high cost of molds is justified. The techniques are also used to produce parts with tight tolerances and complex contours, even for limited production runs. Curing of the part by this process is achieved while the composite laminate is restrained between two mold surfaces. The male and female parts of the molds are designed to produce a controlled clearance, duplicating the part thickness and contours. The time and pressure and temperature profiles are programmed and continuously monitored during the fabrication run.

Matched-die molding processes cover a variety of moldable materials. The constituents of the composite (fibers, resins, fillers, etc.) and the product form (laminate, preform, bulk, etc.) may vary. This adds versatility to the process and makes it economically attractive. It is, however, most suitable for large-volume production and for parts that require dimensional accuracy.

The process can be described as follows:

1. A preform or stacked prepreg lay-up is placed on one half of the mold. Both the upper and lower halves of the mold are heated (usually independently). The mold temperatures are dictated by

the type of resin used and the part thickness and range from 93°C to 177°C (200°F to 350°F). The heat reduces the resin viscosity, thus ensuring a uniform wetout of all the reinforcing fibers.

2. The mold is closed, and pressure is applied to squeeze out excess air, resulting in a nonporous composite structure. The pressures range from 103 to 6,900 kPa (15 to 1,000 psi), depending on the type of composite, 345 to 1,380 kPa (50 to 200 psi) being the most common.

Composite articles manufactured using this process are usually denser, stronger, less porous, and smoother surfaced than those made by autoclave molding. The process, however, requires the design and fabrication of tools or molds. The type of mold used is closely related to the composite part design, complexity, and production volume. For example, for laminated prepreg material, the forming pressure is high and the mold material must be designed to withstand the molding pressures and the frictional abrasion of repeated molding cycles. For shorter runs or prototype parts in which steel tooling is not economically justified, nonmetallic tooling is commonly used. Usually mineral or glass-filled epoxy molds are constructed. Parts fabricated using these molds can be cured at elevated temperatures of up to 121°C (250°F), and then postcured. For relatively small parts, the process is feasible. For larger parts, however, press-size limitations must be taken into consideration.

The major advantages of composite parts fabricated by compression molding are:

1. High degree of control on part dimensions and on all part surfaces;

2. Uniform and repeatable tight tolerances from part to part;

3. Minimum machining of the part, i.e., ability to drill and trim the part on the press;

4. Ability to form complex contours and intricately shaped composite articles;

5. High degree of automation, which lends itself to high production rates, especially important to the commercial sector (e.g., the automotive industry); and

6. Economic attractiveness because of the versatility of the process to various material forms and compositions.

The compression molding process has several limitations:

1. Composite part size--limited by the availability of equipment of the appropriate size and weight;

2. Need for expensive tooling requiring a long lead time for design and fabrication;

3. Need for composite preform lay-up; and

4. Need for sophisticated processing controls for applied pressure, mold heat-up and cool-down, and curing time.

Filament Winding

The filament winding process is a diversified fabrication method most suitable to the fabrication of structures of revolution, such as pressure vessels, rocket motor cases, and tubular and conical structures (Rosato and Grove, 1964). Continuous reinforcing fibers in the form of single strands or multiple ends or tape are used to achieve maximum strength and stiffness in the fabricated components.

The fiber strands are fed from specially designed creels and wound on a mandrel. The winding fibers may be preimpregnated with resin (dry winding) or wetted by passing the reinforcing fibers through a resin bath. A simplified drawing of this process is shown in Figure IV-4. The winding mandrel is designed to duplicate the component shape. Special winding equipment (with automatic and/or manual controls) positions the wetted fibers in a predetermined pattern dictated by the part design. The winding process continues until the desired number of layers has been applied on the mandrel. Lay-up compaction is achieved by the degree of tension maintained on the fibers during winding. The wound mandrel is then cured in an oven or an autoclave.

There are two basic distinctive winding patterns that can be produced by filament winding:

1. A planar winding in which the winding mandrel remains stationary while the fiber-feed arm rotates about it along the longitudinal axis and

2. A helical winding in which the mandrel rotates continuously while the feed carriage shuttles back and forth at a controlled speed to generate the desired helical angle.

Combinations of filament winding off-axis plies and lay-up of longitudinal tapes to produce helicopter rotor blades are under development.

The tape-winding process (or dry winding) is usually aimed at relatively flat composite structures with limited compound contours. The prime component is the tape-laying head, which automatically cuts the prepreg tape and indexes the adjacent tape. There are several fully automated winding machines in operation at various companies. The capabilities of each machine are dependent on the components being fabricated, production volume, and production rates.

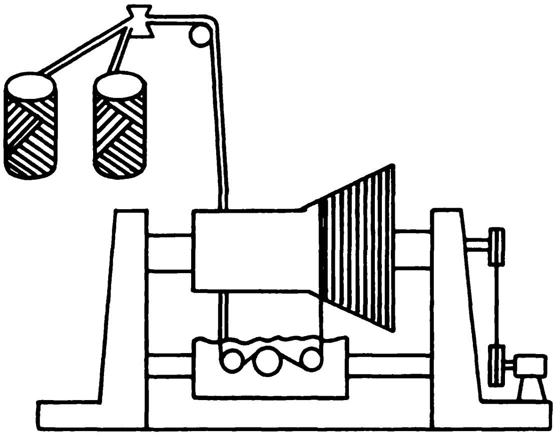


Figure IV-4. Filament winding

The size of composite structures fabricated by filament or prepreg tape winding is limited only by the size of the winding mandrel and the size of the autoclave facilities or curing oven needed for the curing process of the wound structure. Some limitations that require additional advances in the state of technology are:

1. Close control of resin content and distribution. This is especially necessary in the case of wet winding; i.e., control of weight and thickness of the wetted reinforcing fiber as it travels across the winding mandrel.

2. Quality of incoming prepreg tape. For dry winding, the quality and condition of incoming impregnated tape is a major item that must be standardized and controlled. Criteria of acceptance/rejection must be established.

3. Control on winding tension. Any excessive winding tension on the wetted fibers can produce significant differences in resin content betweeen inner and outer layers of the wound composite structure. The winding tension is the most critical limiting factor in controlling and limiting the void content in the wound structure.

4. Control of strand or tape bandwidth. Uneven bandwidth results in weak points occurring at resin-rich areas in the wound structure.

5. Control of filament or tape angles. It is difficult to maintain a precise filament or tape winding angle, especially with very-high-modulus carbon fibers. The problem can be further complicated by geometrical contours of the composite structure being wound.

6. Control of the curing cycle. A well-controlled and monitored cure cycle of the wound structure is essential to control resin flow, minimize fiber movement, and reduce void content in the structure. Nonuniform or incomplete cures usually result in premature failure of the overall structure or localized failure regions.

7. Control of fiber or tape placement. Fiber slippage during the winding process can cause nonuniform fiber placement. This occurs especially at abrupt transitions in contour.

Pultrusion

The pultrusion process is an automated manufacturing method with broad capability for the fabrication of low-cost continuous composite sheets and constant cross-section structural shapes. The process consists of the following stages (Figure IV-5):

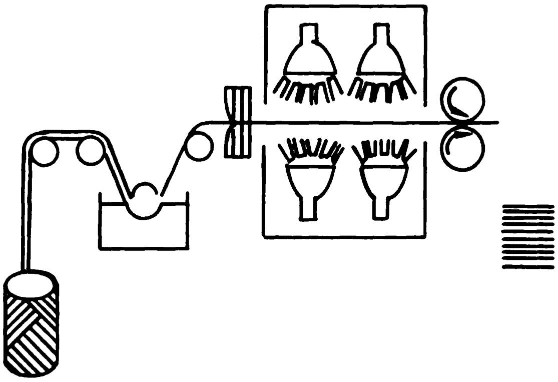


Figure IV-5. Continuous pultrusion

1. Continuous fibers are drawn through a resin bath and a sizing bushing removes entrapped air and excess resin. The reinforcing fibers may be in various forms such as woven fabrics, continuous unidirectional strands or rovings, or chopped or continuous fiber mats. Prepreg tapes or sewn cross-plied strips are also used.

2. The resin-impregnated fibers are then drawn through a shaped die. The die is heated by an external heating unit or by dielectric heating (radio-frequency or microwave frequency). The shape of the stock is set in this manner.

3. The composite article is pulled by a controlled device. At this stage, the part is either completely cured as it leaves the shaping die or it may require further curing in a separate oven.

Channel sections, "Z" sections, and flat bars up to 12.2 m (40 ft) long have been pultruded using several resin systems. The process is currently limited to straight sections of constant cross section; however, some development is needed for producing curved sections and sections of varying cross section (Anonymous, 1979). The process is best suited for relatively fast curing thermosets, such as polyester resin. The process is adaptable to thermoplastic matrices by heating the prepreg to soften the matrix under sufficient pressure to produce adequate ply bonding as the stock passes through the shape dies. The pultrusion is cooled in a chill die to prevent warpage.

Braiding

This is a mechanized textile process in which a mandrel is fed through the center of the machine at a uniform rate and fibers, from moving carriers of the machine, braid about the mandrel at controlled angles. This process is used for channel sections, webs, and circular and box sections with tapering cross section. It is not used with graphite fibers.

Injection Molding

This process is used by the leisure, appliance, and automobile industries for large volumes of parts. It can also be used in the aerospace industry. The process consists of softening a filled thermoplastic (in most cases) or thermosetting material by heating or mechanical working, forcing the softened plastic into a cool mold under high injection pressure, and solidifying the plastic in the mold.

Thermal Expansion Molding

This method consists of wrapping prepreg layers over a rubber core and enclosing the assembly in a metal cavity. Curing pressure is generated by thermal expansion of the rubber mandrel inside the metal restraining tool. Very high pressures, up to 5,500 kPa (800 psi), can be generated if the mass of rubber is not controlled. Tooling is simple, inexpensive, and easily changed. Complex assemblies can be molded in a single cycle. Thus, overall manufacturing costs can be reduced by decreasing the number of parts, eliminating joints, and decreasing assembly and fastening operations.

Honeycomb Sandwich Fabrication

In many structural applications in which both in-plane and flexural stiffness are required, composites are used as skins in sandwich constructions with honeycomb cores. Two methods of fabrication are used. In the first one the composite skins are laid up and cured independently and then bonded to the honeycomb. The second method, known as "cocuring," is a one-step operation in which the skins are laid up on the honeycomb and the whole assembly is cured and bonded together. It has been shown that cocured sandwich constructions have the same structural integrity at a considerable savings in labor. Panels are fabricated by the vacuum/autoclave process.

In the cocuring method, a modified adhesive-type resin matrix is sometimes used for better bonding to the honeycomb. To prevent damage to the skins and honeycomb during cocuring, lower pressures, below 350 kPa (50 psi), are recommended.

Machining Operations

After curing, the composite part may need to be trimmed, cut, milled, routed, drilled, or bored for a variety of structural reasons. Boron reinforced epoxy and Kevlar-reinforced epoxy are specially difficult to machine. Conventional cutting materials, such as tungsten carbide, aluminum oxide, silicon carbide, and steel are softer than boron, which has a hardness of 9.5 on the Mohs scale. Diamond wheels and core drills have been found effective in machining boron-reinforced epoxy. Kevlar composites are even more difficult to machine. The most common practice is contour machining after first sandwiching the Kevlar laminate between two steel or other composite plates. Graphite-reinforced epoxy is generally machined by standard fiberglass machining techniques, but with extra precautions to prevent delaminations. Some less conventional methods, such as laser, water jet, electromagnetic, and ultrasonic cutting have been investigated; however, they have not been adopted on a large scale.

Fastening and Joining

Composite laminates are joined by adhesive bonding, mechanical fastening, or a combination of both. Adhesive bonding is more important because of weight savings and cost reduction. There are two forms of adhesive bonding: cocuring and secondary bonding. The former, when properly done, results in further savings in tools and labor.

The overall bonding technique consists of three steps: selection of adhesive, surface preparation, and bond cycle. Surface preparation is the most important step. Three methods of surface preparation have been used for composites. The first one is the peel ply method in which a heat-sealed and scoured nylon peel ply is applied to the laminate before curing. After curing and possible nondestructive inspection, the peel ply is removed, leaving a surface suitable for bonding. The second method is grit blasting with a fine aluminum oxide powder. The third method is a hand sanding operation followed by a solvent wiping and air drying.

The strength of adhesive bonds is best ascertained through subcomponent testing. Nondestructive ultrasonic techniques are used extensively to ascertain the mechanical integrity of the bond line. These include sophisticated computer-aided pattern recognition schemes and statistical analyses. Such techniques, however, may not always be capable of detecting chemical or physical degradation of the bond line.

Adhesive bonding can be advanced by the development of stronger, tougher adhesives; novel joining methods, such as plastic fusion using thermoplastics; less process-sensitive adhesives; and three-dimensional reinforcement, such as stitching.

Mechanical fasteners are used when high peel stresses are present, when fail-safe characteristics are required, or when periodic disassembly is required. Mechanical fasteners result in high-stress concentrations around bolt holes. These can be alleviated by replacing 0-degree plies around the holes with metallic interleaf springs, or ±45-degree fiberglass or graphite-reinforced epoxy softening strips. More stress and failure analyses, experimental as well as theoretical, are needed to design and evaluate bolted joints in composites.

QUALITY ASSURANCE

Quality control is the most essential task in assuring that fabricated parts meet a level of quality consistent with design requirements. It includes:

1. Acceptance testing of all incoming raw materials by standard quality control procedures, including prime materials such as prepregs and secondary materials such as bag films, sealouts, and bleeder plies;

2. Surveillance of manufacturing operations and processes during part fabrication, including lay-up, curing, and part finishing; and

3. Verification of end product acceptance.

Manufacturing Defects

The enforcement of high-quality standards will eliminate or minimize many defects. The most common fabrication defects and their origins are the following:

1. Delaminations resulting from separation of adjacent layers wthin a multilayered structure because of gas pockets (volatiles) formed during the initial stage of the curing process and entrapped between the cured plies, and because of contamination.
2. Debonds, produced by lack of a bond in a joint area between two separate details. They may result from improper fit of details, failure of the adhesive bond, or contamination of one of the bonded surfaces.
3. Porosity produced from the formation of minute voids in a given area within a solid material. It may be caused by insufficient flow of the resin in the prepreg during the cure cycle or localized excess heating of the resin in the prepreg material during the cure cycle resulting in a foaming action.
4. Resin variations or resin-rich and resin-starved areas. These can occur because of improper control of resin bleeding. Both conditions (resin rich and resin poor) have a significant effect on the performance of the cured composite structure.
5. Fiber damage, such as broken fibers (common to boron) and fiber misalignment.
6. Inclusions, such as separator, backing paper, tape, or other contaminants inadvertently left in the lay-up.

Raw Materials

Raw materials should be obtained from a source that meets standard requirements of engineering and quality assurance. Each batch of prepreg material should be tested and certified by the manufacturer to the requirements of the specifications. Each shipment should be maintained under refrigeration at all times. Samples should be taken and test laminates should be molded by the procedures outlined in the specifications. Physical tests should be conducted to determine resin content, volatile content, and flow. Mechanical qualification testing should be conducted to determine longitudinal flexure, longitudinal tensile, and interlaminar shear strengths.

Process Controls

Close control must be maintained of the number and orientation of the various plies during lay-up. The quality of the tape should be continuously inspected for filament gaps, filament crossover, broken fibers (boron), and foreign particles. The bagging operation should be inspected carefully to insure that proper vacuum is maintained. During curing the temperature and pressure records should be verified by means of permanent charts.

Component Inspection

Cured laminates must be inspected by various nondestructive tests to check for any manufacturing defects, such as delaminations, debonds, porosity, nonuniform fiber distributions, and contaminants. Nondestructive flaw characterization is discussed in detail in Chapter VIII of this report. In addition to the methods discussed in that chapter, simple thickness measurements are indicative of laminate quality. Deviations from the expected thickness can be attributed to a variety of flaws such as delaminations and resin variations.

CONCLUSIONS

1. The properties of composite structures are sensitive to the details of the fabrication process. This correlation, however, is not well established.
2. There are no well-established curing procedures for various prepregs and various part dimensions, such as thick laminates.
3. Despite the introduction of automated equipment, composite fabrication still requires skilled labor and careful quality control.

RECOMMENDATIONS

1. The relationship between various prepreg and processing variables and properties of the finished part should be studied. This should include the relationship between curing cycle and residual stresses and the influence of residual stresses on the behavior of the composite.
2. There is need for more automation in all stages of fabrication, prepreg inspection, prepreg cutting and trimming, and lay-up. This includes the use of alternate material forms, such as sheets preplied by the prepreg manufacturer.
3. Materials and procedures in the bagging and sealing operation can be improved with the introduction of reusable bags, or spray-on-bags.

4. On-line monitoring of the degree of cure should be used with automatic feedback controls. This can include on-line monitoring of outgassing and the correlation with chemical and mechanical changes.

5. More science-based optimized curing procedures that can accommodate variations in component thickness and configuration and can control residual stresses need to be developed.

6. Automated quality control procedures must be established from inspection of incoming materials, through lay-up, curing monitoring and control, and nondestructive evaluation of the finished part.

REFERENCES

Anonymous, "New Technology for Continuous Refinforced Plastics Processing: Curved Pultrusion," Mod. Plast. 56(9), 83, (1979).

Borstell, Hans, private communication, 1980.

Department of Defense (DOD) "Reinforced Plastics," Part I of Plastics for Aerospace Vehicles, MIL-HDBK-17A, Washington, D.C., 1971.

Grumman Aerospace Corp., Bethpage, N.Y., Engineering, Vol. I of Advanced Composite Wing Structures, AFML-TR-70-231, Contract No. F33615-68-C-1301, Air Force Materials Laboratory, December 1970.

Lockheed-Georgia Co., Marietta, Ga., Manufacturing Methods for Thermal Expansion Molding of Advanced Composites, AFML-TR-75-10, Air Force Materials Laboratory, August 1975.

Lockheed-Georgia Co., Marietta, Ga., Advanced Composites Fabrication Guide, Vol. I, Contract No. F33615-75-C-5009, Air Force Materials Laboratory, 1976.

Northrop Corp., Hawthorne, Calif., Manufacturing Methods for Cocuring Advanced Composite Materials, Contract No. F33615-71-C-1824, 1971.

Noton, B. "Advanced Composites," Science Base for Materials Processing, NMAB Report No. 355, Washington, D.C., November 1979.

Rockwell International, Los Angeles, Calif., Advanced Composites Design Guide, Vol. III, Third Edition, Contract No. F33615-74-C-5075, Manufacturing Structures Division, Air Force Flight Dynamics Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, 1977.

Rosato, D. V., and C. S. Grove, Jr., Filament Winding: Its Development, Manufacture, and Design, Interscience Publishers, New York, 1964.

Weitsman, Y., "Residual Thermal Stresses Due to Cool-Down of Epoxy-Resin Composites," J. Appl. Mech. 46, 563-567 (1979).

CHAPTER V

UNIDIRECTIONAL PLY PROPERTIES

The unidirectional ply typically represents the basic material form to the designer and fabricator of structural composite material components. For example, composite materials are commonly provided by the materials supplier in the form of thin tapes or sheets of fibers all oriented in one direction, and already impregnated with a suitable polymer, partially cured (B-staged). This is particularly true of the so-called high-performance composites (those containing high-modulus fibers such as graphite). As an alternative, the fabricator may filament-wind the fibers either wet or dry, also resulting in a ply-by-ply buildup of the component part.

The unidirectional ply or lamina of a high-performance composite material typically consists of continuous fibers embedded in a suitable matrix material. The goal is to align the fibers uniformly in one direction, this accurate alignment being a critical parameter governing the values of the resulting ply properties. The less accurately the uniformity of alignment is maintained, the greater the scatter in the resulting physical and mechanical properties.

It is normally both convenient and more efficient to use continuous fibers rather than unidirectionally oriented discontinuous ones. Handling and accurate alignment of continuous fibers is much easier. Also, continuous fibers carry loads more efficiently and reduce internal stress concentrations induced at fiber ends. Occasionally these advantages are outweighed by still others associated with the use of discontinuous fibers. For example, certain short fibers called "whiskers" can be produced with extremely high moduli and strengths (Levitt, 1970). Being very short, often only a few hundred micrometers long, alignment becomes a major problem. With the fabrication technology presently available, if high performance is the goal, continuous fibers rather than whiskers are normally used.

In many commercial applications where performance must be balanced against reduced fabrication cost, fabrics are frequently used. Typically these fabrics are also thin sheets, but with fibers woven in two orthogonal directions, perhaps with more fibers in one direction than the other (bias weave). The tortuous path of the fibers across the fabric and the lower fiber volume leads to reduced composite strength and stiffness. However, because the fabric ply is a specially orthotropic lamina, as is the unidirectional ply, the same characterization techniques can be used. Emphasis in this section will be on the characterization of the unidirectional ply.

Thus, in the present discussion, the term unidirectional ply will imply a lamina containing carefully aligned, continous fibers. The resultant ply is highly anisotropic (orthotropic), very strong and stiff in the fiber direction, but very low in strength and stiffness in the transverse directions. Correspondingly, the shear strength and stiffness parallel to the fiber direction are also very low.

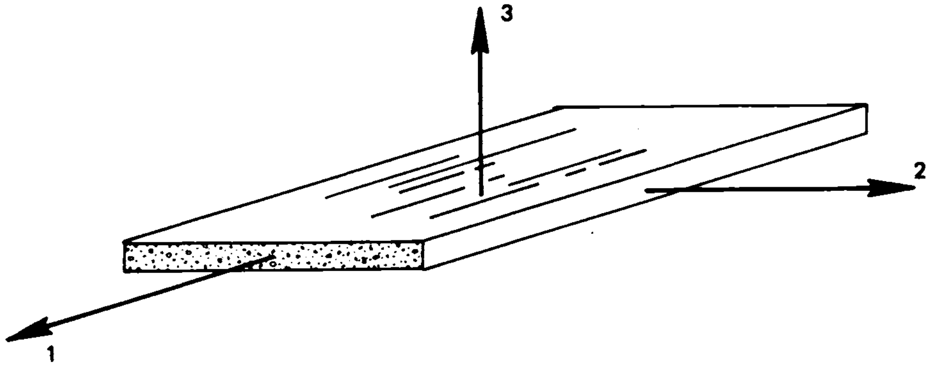
The low transverse normal and longitudinal shear strengths of the unidirectional composite lamina are due both to the relatively low strength of most organic (polymer) matrix materials, including polyesters, epoxies, and polyimides, and to the stress and strain concentrations created by the typically higher modulus fibers embedded in them. The interacting stress fields in the matrix between closely spaced fibers amplify these stress concentrations. Thus, fiber volume and local fiber packing geometry have a significant influence on the off-axis strength properties. Voids and similar imperfections in the matrix material also create and amplify local stresses.

Because of the small thickness of an individual ply, it is customary to lay up multiple plies into a unidirectional laminate for property characterization tests. A photomicrograph of a transverse cross section of a well-prepared unidirectional composite laminate will indicate little or no evidence of the individual plies. Correspondingly, experimental data indicate that the properties of the multi-ply unidirectional laminate are representative of those of the basic material ply.

By specifying the number of plies required, and their individual material types, thicknesses, and orientations, the designer can achieve the multiaxial strengths and stiffnesses required. Thus the designer need know little about fiber and matrix properties, or how the unidirectional ply was made. These latter areas are the realm of the materials engineer and polymer chemist. How the designer uses the unidirectional ply properties is discussed in Chapter VI.

PROPERTIES

The following sketch of a unidirectional ply indicates the coordinate system that will be used in this section in defining specific ply properties.



That is, direction 1 is the direction of the fiber reinforcement; direction 2 is in the plane of the ply, transverse to the fiber direction; and direction 3 is normal to the plane of the ply.

If the unidirectional ply is to be the basic building block of the designer of composite materials, it must be fully characterized. The definition of fully characterized has been continually broadened during the past decade, as applications have increased; and with their increase has come an increase in the demands on the material. Because most prior uses have been in high mechanical (structural) performance applications, the emphasis has been on strength and stiffness. However, newer applications require knowledge of many additional properties. The following list includes some of these properties; the symbols are commonly accepted but are by no means standardized within the composites community:

E_{11} = longitudinal stiffness (tension and compression),

E_{22} = transverse stiffness (tension and compression),

G_{12} = longitudinal shear stiffness,

G_{23} = transverse shear stiffness

ν_{12} = major Poisson's ratio (tension and compression),

ν_{21} = minor Poisson's ratio (tension and compression),

S_{11} = longitudinal strength (tension and compression),

S_{22} = transverse strength (tension and compression),

S_{12} = longitudinal shear strength,

S_{23} = transverse shear strength,

e_{11} = longitudinal strain to failure (tension and compression),

e_{22} = transverse strain to failure (tension and compression),

e_{12} = longitudinal shear strain to failure,

α_{11} = coefficient of longitudinal thermal expansion,

α_{22} = coefficient of transverse thermal expansion,

β_{11} = coefficient of longitudinal moisture expansion,

β_{22} = coefficient of transverse moisture expansion,

D_{11} = longitudinal moisture diffusion coefficient,

D_{22} = transverse moisture diffusion coefficient,

M_m = maximum moisture content,

K_{11} = longitudinal thermal conductivity,

K_{22} = transverse thermal conductivity,

C_p = specific heat capacity,

U_{11} = longitudinal impact energy absorption (tension and compression),

U_{22} = transverse impact energy absorption (tension and compression),

U_{12} = longitudinal shear impact energy absorption,

$J_{11}(t)$ = longitudinal creep compliance (tension and compression),

$J_{22}(t)$ = transverse creep compliance (tension and compresson),

$J_{33}(t)$ = shear creep compliance,

$E_{11}(t)$ = longitudinal relaxation modulus (tension and compression),

$E_{22}(t)$ = transverse relaxation modulus (tension and compression),

$G_{12}(t)$ = shear relaxation modulus,

E'_{11} = longitudinal storage modulus (tension and compression),

E'_{22} = transverse storage modulus (tension and compression),

G'_{12} = shear storage modulus,

E''_{11} = longitudinal loss modulus (tension and compression),

E''_{22} = transverse loss modulus (tension and compression),

G''_{12} = longitudinal shear loss modulus,

T_g = glass transition temperature,

Longitudinal fatigue (tension and/or compression), Transverse fatigue (tension and/or compression),

Longitudinal shear fatigue,

Creep rupture,

Longitudinal dielectric constant,

Transverse dielectric constant,

Longitudinal electrical conductivity,

Transverse electrical conductivity,

Density,

Surface hardness,

Wear resistance,

Lubricity,

Chemical resistance, and

Resistance to ultraviolet and radiation..

Many of these properties, particularly strength, are strong functions of temperature, moisture content, and other environmental exposures, including chemicals and ultraviolet radiation. Thus, if such environments are to be designed for, each of these properties must be characterized in the environment of interest.

Characterization Methods

Characterization methods for determining the properties of the unidirectional ply are not yet adequately standardized. (Some of the physical properties, e.g., density and thermal expansion, can be measured in the same manner as they are for conventional, homogeneous, isotopic materials.) The primary difficulty stems from the high degree of anisotropy exhibited by the unidirectional material (Ives et al., 1971; Whitney, 1978).

Longitudinal tensile strength determination (and hence also longitudinal strain to failure) is plagued by difficulties in gripping the specimen. End tabs become mandatory. High axial loads are then transferred via a shear mechanism through an adhesive layer between specimen and end tab. The low shear strengths of both the composite and the adhesive make the tabbing design critical. Reducing the specimen cross-sectional area in the gage length is not always beneficial; the high anisotropy then promotes longitudinal shear failure in the fillet regions, and up into the tabs. Also, the specific problems encountered in tensile testing are not the same as those of compressive testing.

Compressive testing of the relatively thin, but strong, specimen introduces the problem of preventing gross buckling failures (Shuart and Herakovich, 1978). Currently two approaches are taken. Either the specimen length-to-thickness ratio is kept small, e.g., on the order of 2 to 5, or the specimen is laterally restrained. The so-called Celanese test method (American Society for Testing and Materials [ASTM], 1975) or a variation, the Illinois Institute of Technology Research Institute (IITRI) test method (Hofer and Rao, 1977), are examples of the first approach. The overall length of the test specimen is 14 cm (5-1/2 in.), but 6.3-cm (2-1/2-in.) tabs are bonded on each end, leaving an untabbed central length of only 1.3 cm (1/2 in.). The tabbed regions are then supported in wedge grips over their entire length. The central gage section is designed not to buckle. A simple short block, either circular or rectangular in cross section, compressed between two flat platens, is another example of the first approach. Unlike the Celanese and IITRI tests, where the load is transferred into the gage section via a shear mode, the load is introduced into the short block directly by compressive forces at the ends. This leads to localized (end effect) failures such as specimen brooming. The incorporation of some type of lateral restraint is mandatory because large specimen gage length-to-thickness ratios are used (Ryder and Black, 1977; Shuart and Herakovich, 1978). Although many methods of providing lateral restraint are currently in use, the common purpose is to prevent gross buckling. Typically this forces the material into a local buckling (microbuckling) mode. Perhaps the major disadvantage of using lateral restraint is the possibility of disturbing the desired uniaxial stress state.

The measurement of the major Poisson's ratio is reasonably straightforward. Accurate determination of the minor Poisson's ratio is usually more difficult because of its smaller magnitude.

In theory, the determination of the shear strength and stiffness of a unidirectional composite is straightforward. A thin-walled tube, with the fibers all oriented axially or circumferentially, is subjected to axial torsion, introducing the desired uniform pure shear stress (Chiao et al., 1977). However, the expense of fabricating tubes and the difficulty of gripping them without damage make this a less attractive test method. A solid rod with the fibers oriented in the axial direction can be used instead (Adams and Thomas, 1969). This solid rod is simple to fabricate and simple to test, and, as with the thin-walled tube, both shear strength and stiffness are obtained. It has the disadvantage, however, that the shear stress is nonuniform, varying from zero at the center of the circular cross section to a maximum at the outer surface. If the material response is nonlinear, this stress distribution is nonlinear. This nonuniformity of stress can be taken into account in calculating strength and stiffness (Marin, 1962), but it does detract from the test method.

Many other shear test methods are being used at present, and new ones, or variations of old ones, are continually being proposed. Most of these methods suffer from one or both of two major deficiencies, i.e., a pure stress state is not induced, or both strength and modulus cannot be determined. Familiar shear test methods, such as short beam shear (ASTM, 1976), rail shear (Whitney et al., 1971), plate twist (Tsai, 1965), Iosipescu (Iosipescu, 1967), off-axis tension (Chamis and Sinclair, 1976), $\pm 45^{\circ}$ coupon (Petit, 1969), and notched specimen (Loveless and Ellis, 1977) are all examples.

In applying many of the test methods discussed in this section, some means of measuring strains is necessary. At present, two primary methods are used: strain gages and strain gage extensometers. Difficulties are encountered in testing moisture-conditioned specimens. Bonding the strain gage to the wet surface after conditioning is a problem; and the specimen will lose moisture during this process. If the gage is applied prior to moisture conditioning, it may debond during the long-term moisture exposure. Strain gage extensometers eliminate these problems. However, most extensometers have a 2.5-cm (1-in.) gage length, or a 1.3-cm (1/2-in.) gage length when space is a limitation. Compared to strain gages, which can have gage lengths of 1.6 mm (1/16-in.) or less if necessary, extensometers occupy considerable space. They are also more limited in terms of the specimen geometry they can be used on.

Because the coefficient of transverse thermal expansion of a unidirectional composite is typically greater than $10^{-5}/^{\circ}C$ ($5.5 \times 10^{-6}/^{\circ}F$), it can be measured readily by conventional methods such as by a quartz tube dilatometer or strain gages (ASTM, 1971). However, because the slightly negative coefficient of axial thermal expansion and high axial modulus of fibers such as graphite and Kevlar tend to offset the highly positive coefficient of thermal expansion and low elastic modulus of the polymer matrix, the resulting coefficient of axial thermal expansion of a graphite- or Kevlar-reinforced epoxy unidirectional composite can be very small (typically slightly negative). Often it is necessary to measure values in the range of $10^{-8}/^{\circ}C$ ($5.5 \times 10^{-9}/^{\circ}F$). Accurate measurement of the correspondingly small displacements requires special equipment. Currently, optical systems are often used (Freund, 1975; Goggin and Raquin, 1971).

Similar comments apply to the measurement of moisture expansion coefficients. Transverse measurements are not difficult to make, the displacements being relatively large. Longitudinal values are very small (positive), the large moisture expansion of the polymer matrix being restrained by the zero moisture expansion of the much stiffer fibers. If a laser and mirror system is used, it must operate in the moist environment. A somewhat unique consideration when making moisture expansion measurements is maintaining an equilibrium state. Because the moisture diffusion coefficient is typically very small, a long time is required to achieve even a reasonable approximation of moisture equilibrium (Shen and Springer, 1976). That is, the possibility of moisture gradients existing in the material while measurements are being made must be considered. The corresponding thermal gradient problem is not significant because the time to achieve thermal equilibrium is typically measured in minutes rather than in months as for moisture equilibrium.

Measurements of moisture diffusion coefficients and thermal conductivities present no major difficulties other than the need to account for the material anisotropy.

Determination of the impact resistance of composite materials, including unidirectional composites, remains an essentially unresolved area (Adams, 1976). Traditional test methods such as Charpy and Izod impact, originally developed for homogeneous, isotropic metals (ASTM, 1972), have been found to be of limited utility. Designed to induce flexural failure modes (in metal), the failure mode when testing a composite changes from one material to another, and changes with fiber orientation. Thus, the energy absorption values obtained are difficult to interpret. Low-level impacts (impact intensities less than those necessary to cause fracture, or even visible damage) are known to degrade some composite materials (Adams and Perry, 1977; Hancox, 1971; Simon, 1973). Yet the mechanisms governing this degradation are largely unknown.

Preliminary efforts have been made to develop a tensile impact test to induce a simple (uniaxial tensile) stress state (Benson, 1979; Plenger, 1975). This will make the resulting impact data easier to interpret. If successful, this could eventually lead to the development of compression and shear impact tests as well. That is, unidirectional composite materials may be characterized in impact in a manner similar to current static properties determinations.

While creep properties of composites are better understood than impact properties, relatively little data are currently available (Schapery et al., 1973; Soliman, 1969; Sturgeon et al., 1976). With the increasing use of composites at high temperatures and stress levels, and in dimensionally critical applications, interest in creep response is increasing significantly. This will undoubtedly stimulate more experimental work.

The fatigue properties of composite materials have been characterized (Hancock, 1975; Reifsnider and Lauraitis, 1977); compression-compression fatigue is of greatest concern. However, while certain fatigue properties are available, the mechanism of fatigue failure is not adequately understood. How cracks initiate and propagate under various loading modes is largely unknown. This is in contrast to homogeneous materials such as the metals in which crack initiation and propagation can be readily identified and classified

(Boyer, 1975). The anisotropic, nonhomogeneous nature of composites makes the failure mode extremely sensitive to the loading mode; slight changes in the anisotropy of one composite material relative to another can result in totally different failure modes for identical loading configurations.

Until recently, there has been little emphasis on dynamic properties of composite materials. However, applications to sporting goods and, more recently, to automobiles, have generated significant interest in determining the damping properties of various composite materials. It is generally stated that composites exhibit good damping; but few data are actually available. Thus interest is increasing in developing acceptable test methods, and in generating supporting data (Bert and Clary, 1974; Tauchert, 1974). This will undoubtedly lead to an interest in more fully characterizing all the dynamic properties of unidirectional composites.

Biaxial testing of the unidirectional ply is also needed to define the failure envelope of the material. This will include fatigue loadings as well as static and dynamic loadings.

There are a number of physical properties, e.g., dielectric constants, electrical conductivities, chemical resistance, and wear resistance, that, while perhaps not well characterized, can be readily measured using standard test methods. Many of the current composite materials simply have not yet been used in applications in which certain of these properties are critical. Thus, there has been less urgency to characterize them.

Limitations and Needs

Perhaps the greatest limitations at present to the adequate characterization of organic matrix composites are the lack of suitable test methods and an incomplete understanding of failure mechanisms. Although test methods development has been a topic of major interest to the composites community for many years, only modest progress has been made in establishing standard test methods. It appears that this is going to continue to be a gradual, evolutionary development process. Thus, while there is an obvious need for standard test methods, it is not expected that this will occur in the near future. It is encouraging, however, that increasing emphasis is being placed on fundamental studies of failure modes associated with the various test methods being developed.

Voluntary standards groups such as ASTM, the current pacesetter in test methods standards development for composite materials, will probably continue to take the lead in this area. Important contributions can also be expected from government agencies, particularly in the continued development of the Advanced Composites Design Guide by DOD and NASA and MIL-HDBK-17A by the Army.

While the current plea is for more data with which to characterize organic matrix composites, many of the data that do exist are not fully usable because they were obtained using questionable test methods. Rather than continue to generate such data, it will be more beneficial to emphasize the use of common test methods, selected from the best currently available, while continuing to develop improved test methods. In the interim, much can be done to supplement the available experimental data by using analytical methods of predicting composite properties based upon known or estimated constituent properties. As an indication of the standardized test methods currently available, the Bibliography to this chapter lists the ASTM Standards that have either been developed specifically for composite materials or are commonly used even through originally developed for homogeneous materials.

CHARACTERIZATION APPROACHES

Characterization of the unidirectional ply can be addressed from two aspects, viz., determination of the physical and mechanical properties of the ply as a function of fiber and matrix type, and determination of the influence of compositional variations of specific constituents on ply properties.

Given a fiber of nominal properties and an organic matrix of specified composition, the physical and mechanical properties of the resulting unidirectional ply can be determined. The various properties to be determined and the available test methods are outlined earlier in this chapter in the section entitled "Properties." Ideally it would be desirable to measure all the physical and mechanical properties experimentally, using well-established test methods and procedures. As previously discussed, however, test methods for composite materials are not well developed, and different test specimen configurations result in different values. Also, to characterize fully a unidirectional ply, a very large number of properties must be measured. This can result in a very extensive and costly test program.

Thus, the approach of using theoretical methods to predict certain of these properties based upon constituent properties is becoming more and more widely accepted. The available predictive methods are becoming more refined, permitting more comprehensive modeling and more accurate results.

Experimental Methods

Some of the basic problems associated with the characterization of unidirectional composites are discussed in the earlier subsection entitled "Characterization Methods." Because test methods are not well standardized, most aerospace-oriented groups have tended to develop their own procedures, which are modified frequently as new techniques emerge. On the other hand, those industry groups that have only recently become interested in composite materials have tended to look to the standards groups such as ASTM whenever possible. It should be noted that ASTM has established several individual test method standards for composite materials, based primarily on extent of use rather than total suitability of the particular method.

Up to the present time it has been commonplace to measure only those properties of particular interest to the specific application, and to report only general test conditions. Thus, the literature is filled with experimental results that are difficult to interpret, and insufficiently complete to be useful to others. In fact, most experimental work on characterization of properties has been performed as a relatively minor part of a large applications program. Although the need for programs specifically to generate experimental data has been generally recognized, funding has not normally been provided. This is somewhat understandable because the composite materials themselves have almost continuously been replaced by improved systems, making previously generated data obsolete. Recently, however, the number of primary materials suppliers has stablized somewhat, and a selected few fiber-reinforced matrix systems have emerged to capture a large fraction of the market. Examples include T300/5208, AS/3501-6, and GY70/930 graphite-fiber reinforced epoxy composite materials. It may now, therefore, be practical for government agencies to promote the thorough characterization of selected systems.

The preferred procedure would be to purchase prepreg to a well-defined specification, fabricate unidirectional panels using a specific procedure, inspect by means of established quality control methods, and then prepare specimens and perform tests following a well-established standard. Results should then be reported in a prescribed format and given wide dissemination by including them in established publications, such as the Advanced Composites Design Guide and MIL-HDBK-17A.

Theoretical Predictions

The experimental data generated as defined in the preceding subsection would be for specific fiber and matrix combinations. The problem remains of determining the properties of other combinations, particularly for newly emerging fibers and matrix materials. It is suggested that existing theoretical methods, and new methods yet to be developed, could be used more extensively than at present to predict the properties of these materials. This would provide a much more economical means of making preliminary evaluations. Also, it could give better insight as to why one material might perform better than another under particular environmental and loading conditions.

At present, most of the theoretical analysis methods are in the hands of a very few investigators. These analyses often have been developed as part of a company in-house program, with no attempt being made to disseminate them, or as part of a government-sponsored basic research program, with little emphasis on carrying the work through to a well-documented, user-oriented end product. As a result, some very creative work by individual investigators has fallen into obscurity. A mechanism should be established to encourage investigators to promote their work and to prepare it for general use.

Early works published in the open literature that remain today as examples of the many diverse approaches available include those by Hill (1964), Pickett (1968), Hashin and Rosen (1964), Hashin (1972), and Chen and Cheng (1967).

The problem of disseminating significant works has become even more severe in recent years as numerical methods of analysis have become prevalent. The combination of more complex problems to be analyzed and the availability of digital computers has made the use of numerical methods a logical trend. However, for someone else to make efficient use of a large-scale computer program, the program must be fully developed and carefully documented. The developers of the present edition of the Advanced Composites Design Guide took a step in this direction by publishing several composite materials analysis programs. However, an adequate method of disseminating copies of these computer programs was not set up.

In terms of unidirectional ply characterization, the so-called micromechanics analyses are particularly applicable.

Compositional Variations

Of perhaps equal importance with the influence of different constituent materials on undirectional ply properties is the influence of variations in the composition of a particular composite, or its constituents. For example, the user needs to know how a variation in fiber volume content, either within or out of specification, will influence various properties of the unidirectional ply. This information will probably even be the basis of the specification. In a similar fashion, a variation in axial modulus of the fiber, or strain to failure of the organic matrix, will also influence the composite ply properties. This influence must be quantified for quality control and performance prediction purposes. This can be done either experimentally or theoretically.

The use of experimental methods to determine the influence of compositional variations is obviously the most direct approach and should be used whenever practical. Two major difficulties arise, however. First, it may not always be practical, or even possible, to introduce deliberately and controllably specific compositional variations. Second, the number of possible variations can become quite large. Because even determining the basic material properties of a unidirectional composite represents a significant effort, repeating this series of tests for even a few variations can be prohibitive.

It is perhaps in this aspect of materials characterization that theoretical analyses are most attractive. The base case experimental data can be used to verify the theory or to indicate its limitations. Compositional variations of interest can then be studied with relatively little effort, and at minimal cost, using the computer simulation approach. Any particularly severe anomaly or unexpected prediction can then be verified experimentally if the associated compositional variation can be physically duplicated.

SUMMARY OF THE STATE OF THE ART

The characterization of the unidirectional ply properties of organic matrix composites presently suffers from the lack of adequate test methods, continually evolving materials availability, and the high cost of conducting the large number of physical and mechanical tests required to characterize fully the composite. More extensive and systematic use of theoretical analyses could alleviate some of these current limitations if these analyses were further developed and put into forms convenient to the potential user.

It appears that the development of adequate test methods is going to continue to be a slow evolutionary process. On the other hand, the types of composite materials in most common use appear to be stabilizing somewhat after many years of almost continual change as improved fibers and matrix materials were continually introduced. Thus, it may be possible to concentrate on a few key material systems and attempt to characterize them as completely as possible.

The high cost of performing any extensive series of experimental tests cannot be avoided, whether conventional materials or composites are being characterized. Thus, a few representative material systems should be selected for extensive testing and development of standards. This is analogous to the standardization of selected metal alloy compositions: a vast number of aluminum or steel alloy compositions could be produced, if it were desirable to do so.

Reasonable progress is being made in the development of theoretical analyses for predicting unidirectional ply properties, although much more could be done, and at a more rapid rate, if greater emphasis were placed in this area. At present, most of the work is being done by only a few investigators, with most of the emphasis placed on research aspects rather than on the problems of preparing the analyses and associated computer programs in a form readily usable by others. Little attempt is being made to disseminate these analyses.

CONCLUSIONS

1. The unidirectional ply represents the basic building block from which a composite structure is constructed.

2. Currently, only very selected properties of the unidirectional ply are experimentally characterized routinely.

3. More sophisticated design requirements are rapidly requiring more complete characterization of this basic building block. Examples include temperature and moisture effects, impact, viscoelastic response, damping capacity, fatigue behavior, and determination of failure modes.

4. Extensive experimental characterization, especially of the mechanical properties of the unidirectional ply, for each fiber and matrix combination, fiber volume, etc., is desirable.

5. Analytical methods of predicting unidirectional ply properties, incorporating finite element solution techniques, are becoming more reliable and usable. These micromechanical analyses permit the study of compositional variations with relatively little effort, by making a series of routine computer runs.

RECOMMENDATIONS

1. The continued development of test methods suitable for characterizing the unidirectional ply properties of organic matrix composites should be encouraged.

2. Emphasis should be placed on the selection for complete characterization of a few composite material systems to be established as standards.

3. Theoretical analyses should be presented in forms convenient for general use. Micromechanics computer programs should be standardized and disseminated as they become available and used to predict unidirectional ply properties when experimental data are not available and to aid and guide material scientists and engineers in developing improved acceptance criteria.

4. Emphasis should be placed on the development of additional micromechanical analyses and related computer programs emphasizing rigorous approaches and encouraging developments in relatively unexplored areas such as environmental effects, viscoelastic response, dynamic loading, fracture mechanics, and failure mechanisms.

5. Fracture studies using experimental techniques to identify fracture initiation and failure modes should be encouraged.

REFERENCES

Adams, D. F., *Composite Materials: Testing and Design*, ASTM STP 617, American Society for Testing and Materials, Fourth Conference; Philadelphia, 1976, p. 409.

Adams, D. F., and J. L. Perry. *J. Eng. Mater. Technol.*, *99*, 257 (1977).

Adams, D. F., and R. L. Thomas, *Tex. Res. J.*, *39*, 339 (1969).

American Society for Testing and Materials, *Linear Thermal Expansion of Rigid Solids with a Vitreous Silica Dilatometer*, ASTM Standard E 228-71, Philadelphia, 1971.

American Society for Testing and Materials, *Notched Bar Impact Testing of Metallic Materials*, ASTM Standard E 23-72, Philadelphia, 1972.

American Society for Testing and Materials, *Test for Compressive Properties of Oriented Fiber Composites*, ASTM Standard D 3410-75, Philadelphia, 1975.

American Society for Testing and Materials, *Apparent Horizontal Shear Strength of Reinforced Plastics by Short Beam Method*, ASTM Standard D 2344-76, Philadelphia, 1976.

Benson, R. A., *Instrumented Tensile and Charpy Impact of Composite Materials*, Master of Science thesis, Department of Mechanical Engineering, University of Wyoming, 1979.

Bert, C. W., and R. R. Clary, *Composite Materials: Testing and Design*, ASTM STP 546, American Society for Testing and Materials, Philadelphia, 1974, Third Conference, p. 250.

Boyer, H. E., ed., *Failure Analysis and Prevention*, Vol. 10 of *Metals Handbook*, American Society for Metals, Metals Park, Ohio, 1975.

Chamis, C. C., and J. H. Sinclair, *10° Off-Axis Tensile Test for Interlaminar Shear Characterization of Composites*, NASA TN D-8215, National Aeronautics and Space Administration, Cleveland, 1976.

Chen, C. H., and S. Cheng, *J. Compos. Mater.* *1*, 30 (1967).

Chiao, C. C., R. L. Moore and T. T. Chiao, *Composites*, *8*, 181 (1977).

Freund, N. P., *Composite Reliability*, ASTM STP 580, American Society for Testing and Materials, Philadelphia, 1975, p. 133.

Goggin, W. R., and R. A. Raquin, *Image Technol.*, *13*, 6 (1971).

Hancox, N. C., *Composites*, *2*, 41 (1971).

Hancock, J. R., *Fatigue of Composite Materials*, ASTM STP 569, American Society for Testing and Materials, Philadelphia, 1975.

Hashin, Z., *Theory of Fiber Reinforced Materials*, NASA CR-1974, National Aeronautics and Space Administration, Washington, D.C., 1972.

Hashin, Z., and B. W. Rosen, *J. Appl. Mech.*, *31*, 223, (1964).

Hill, R., *J. Mech. Phys. Solids*, *12*, 199 (1964).

Hofer, K. E., Jr., and P. N. Rao, *J. Test. Eval.*, *5*, 278 (1977).

Iosipescu, N., *J. Mater.*, *2*, 537 (1967).

Ives, G. C., J. A. Mead, and M. M. Riley, *Handbook of Plastics Test Methods*, Butterworths Science Publishers, London, 1971.

Levitt, A. P., *Whisker Technology*, John Wiley and Sons, New York, 1970.

Loveless, H. S., and J. H. Ellis, *J. Test. Eval.*, *5*, 369 (1977).

Marin, J., *Mechanical Behavior of Engineering Materials*, Prentice-Hall, Inc., 1962.

Petit, P. H., *Composite Materials: Testing and Design*, ASTM STP 460, American Society for Testing and Materials, Philadelphia, 1969, p. 83.

Pickett, G., *Fundamental Aspects of Fiber Reinforced Plastic Composites*, R. T. Schwartz and H. S. Schwartz, eds., Chapter 2, Wiley-Interscience, New York, 1968.

Plenger, J. H., *Tensile and Charpy Impact Testing of Unidirectional Composite Materials*, Master of Science thesis, Department of Mechanical Engineering, University of Wyoming, 1975.

Reifsnider, K. L., and K. N. Lauraitis, ed., *Fatigue of Filamentary Composite Materials*, ASTM STP 636, American Society for Testing and Materials, Philadelphia, 1977.

Ryder, J. T., and E. D. Black, *Composite Materials: Testing and Design*, ASTM STP 617, Fourth Conference, American Society for Testing and Materials, Philadelphia, 1977, p. 170.

Schapery, R. A., S. W. Beckwith, and N. W. Conrad, *Studies on the Viscoelastic Behavior of Fiber-Reinforced Plastic*, AFML-TR-73-179, Air Force Materials Laboratory, 1973.

Shen, C. H., and G. S. Springer, *J. Compos. Mater.*, *10* 2(1976).

Shuart, M. J., and C. J. Herakovich, An Evaluation of the Sandwich Beam in Four-Point Bending as a Compressive Test Method for Composites, NASA Technical Memorandum 78783, National Aeronautics and Space Administration, Hampton, Va., 1978.

Simon, R. A., Proceedings of the 28th Annual Conference of the Reinforced Plastics/Composites Institute, Society of the Plastics Industry, New York, N.Y., 1973.

Soliman, F. Y., Composite Materials: Testing and Design, ASTM STP 460, American Society for Testing and Materials, Philadelphia, 1969, p. 254.

Sturgeon, J. B., R. I. Butt, and L. W. Larke, Creep of Carbon Fibre Reinforced Plastics, Technical Report 76178, Royal Aircraft Establishment, Farnborough, Hants, United Kingdom, 1976.

Tauchert, T. R., J Compos. Mater., 8, 195 (1974).

Tsai, S. W., J. Eng. Ind., 87, 315 (1965).

Whitney, J. M., D. L. Stansbarger, H. B. Howell, J. Compos. Mater., 5, 24 (1971).

Whitney, J. M., ed., Analysis of the Test Methods for High Modulus Fibers and Composites, ASTM STP 521, American Society for Testing and Materials, Philadelphia, 1978.

BIBLIOGRAPHY

Chemical Resistance

ANSI/ASTM D 543-67 (reapproved 1978), *Resistance of Plastics to Chemical Reagents*.

ANSI/ASTM C 581-74 (reapproved 1978), *Chemical Resistance of Thermosetting Resins Used in Glass Fiber Reinforced Structures*.

Creep

ANSI/ASTM D 2991-71 (reapproved 1978), *Stress-Relaxation of Plastics*.

ANSI/ASTM D 2990-77, *Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics*.

Electrical Properties

ANSI/ASTM D 149-75, *Dielectric Breakdown Voltage and Dielectric Strength of Electrical Insulating Materials at Commercial Power Frequencies*.

ANSI/ASTM D 150-78, *A-C Loss Characteristics and Permittivity (Dielectric Constant) of Solid Electrical Insulating Materials*.

Fatigue

ANSI/ASTM D 671-71 (reapproved 1978), *Flexural Fatigue of Plastics by Constant-Amplitude-of-Force*.

ANSI/ASTM D 3479-76, *Tension-Tension Fatigue of Oriented Fiber Resin Matrix Composites*.

Impact

ANSI/ASTM D 1822-68 (reapproved 1973), *Tensile-Impact Energy to Break Plastics and Electrical Insulating Materials*.

ASTM E 23-72, *Notched Bar Impact Testing of Metallic Materials*.

ANSI/ASTM D 256-78, *Impact Resistance of Plastics and Electrical Insulating Materials*.

ANSI/ASTM D 3029-78, *Impact Resistance of Rigid Plastic Sheeting or Parts by Means of Tup (Falling Weight)*.

Mechanical Testing

ANSI/ASTM D 790-71 (reapproved 1978), *Flexural Properties of Plastics and Electrical Insulating Materials*.

ANSI/ASTM D 3410-75, *Test for Compressive Properties of Oriented Fiber Composites*.

ANSI/ASTM D 2344-76, *Apparent Horizontal Shear Strength of Reinforced Plastics by Short Beam Method*.

ANSI/ASTM D 3039-76, *Tensile Properties of Oriented Fiber Composites*.

ANSI/ASTM D 3518-76, *In-Plane Shear Stress-Strain Response of Unidirectional Reinforced Plastics*.

ANSI/ASTM D 638-77a, *Tensile Properties of Plastics*.

ANSI/ASTM D 695-77, *Compressive Properties of Rigid Plastics*.

Physical Properties

ANSI/ASTM D 792-66 (reapproved 1975), *Specific Gravity and Density of Plastics by Displacement*.

ANSI/ASTM D 1505-68 (reapproved 1975), *Density of Plastics by the Density-Gradient Technique*.

ANSI/ASTM D 2734-70 (reapproved 1976), *Void Content of Reinforced Plastics*.

ASTM D 3355-74, *Fiber Content of Unidirectional Fiber/Polymer Composites*.

Thermal Conductivity

ANSI/ASTM C 177-76, *Steady-State Thermal Transmission Properties by Means of the Guarded Hot Plate*.

Thermal Expansion

ANSI/ASTM D 696-70 (reapproved 1978), *Coefficient of Linear Thermal Expansion of Plastics*.

ASTM E 228-71, *Linear Thermal Expansion of Rigid Solids with a Vitreous Silica Dilatometer*.

Thermal Properties

ANSI/ASTM D 648-72 (reapproved 1978), *Deflection Temperature of Plastics under Flexural Load*.

Wear Resistance

ANSI/ASTM D 1242-56 (reapproved 1975), Resistance of Plastic Materials to Abrasion.

ANSI/ASTM D 673-70 (reapproved 1976), Mar Resistance of Plastics.

CHAPTER VI

DESIGN AND ANALYSIS

To produce a reliable and efficient composite primary structure, a designer must resolve a number of challenges, challenges that if not unique to filamentary composites, are more pronounced than those encountered in the study of other high-performance structural materials. The most obvious of these is thermomechanical anisotropy, which, as seen in the previous chapter, manifests itself in directionally dependent ply properties. Less obvious but more difficult to accommodate is low ductility, which causes concerns about stress concentrations and notch sensitivity. A third problem, which filamentary composites share with unreinforced polymers, is that of time-temperature-moisture enhanced failure of a loaded structure. Fourth, is variation in properties, or, more explicitly, the specification and certification of final part properties. The final problem is high cost, which is often coupled to the previous four. For example, inadequate certification and characterization reduce designer confidence and result in excessive safety margins, premature replacement, overspecification, or unnecessary use of expensive material, each of which increases part cost.

In this chapter we will consider those elements that can be used to deal with these problems of composites and arrive at a successful structural design. Detailed user information on composite design can be found in the Advanced Composites Design Guide (DOD and NASA, 1973), Lubin (1969), and MIL-HDBK-17A (DOD, 1971). Our purpose here is to assess the current status of composite design and to point out those areas in which inadequate predictive techniques of incomplete understanding of material behavior limits the usefulness or acceptance of these strong, lightweight materials. To do this we will first outline the design of a composite structure and then discuss in detail the status of structural mechanics, fabrication, and certification from the viewpoint of the designer.

COMPOSITE STRUCTURAL DESIGN PROCESS

It is difficult to generalize about the design process because it employs a variety of disciplines and depends upon the designer's intuition and creativity. However, two issues are common to most designs: the first concerns the function of the part and the second concerns acceptable cost for the part. The designer's responsibilities include insuring that the part performs as required for an affordable price. For a composite to replace other structural materials, the application would require a unique combination of material properties unattainable in conventional alloys or polymers. This point was illustrated by Scala (1973) and R. Jones (1975).

The design process itself consists of several interrelated and often concurrent activities: structural mechanics, development of suitable fabrication techniques, and certification of the completed structure.

Structural mechanics, which leads to selection and specification of material, properties, geometry, and lamination sequence, is the heart of the composite design process. It usually includes both analytical and experimental studies. A pertinent analysis requires specification of the complete service environment and expected load history of the part (loads, temperatures, service life, moisture, radiation, gases, chemical agents, freeze-thaw, etc.). The second ingredient is an accurate characterization of a unidirectional ply, the basic composite building block. The properties of the ply are fed into the analysis. From this analysis the designer may specify a laminated structure that meets design requirements. It is important that the stress state be completely evaluated because off-axis strength allowables are quite low and may be exceeded. The designer should then identify and reinforce possible trouble spots caused by low material ductility; joints, cutouts, stress-risers, etc. The designer must also try to estimate the reduction in properties caused by fatigue, sustained loading, temperature, or environment. Experimental verification of these estimates will often be required, usually as material property tests.

Concurrent with these activities are the selection and development of suitable fabrication techniques. Although proper processing attempts to minimize part cost by reducing hand lay-ups, tooling, and finishing time, it is equally important to maintain tight controls to reduce property variations. A designer aware of the limitations of various processes can circumvent or substantially reduce the type of problems described in Chapter IV.

The third design activity, certification, consists of formulating a number of specifications to guarantee that the finished part will perform as desired. Quality control of incoming materials (Chapter II), processing specifications (Chapter IV), nondestructive evaluation (Chapter VIII), and proof testing of prototypes are each employed in most designs. Specifications developed with an awareness of the limitations of each component activity have a greater chance for success than others.

From this brief and idealized outline, it should be clear that composite structural design is inherently more complex than that for isotropic materials. The anisotropy, lack of ductility, and high cost of composites, coupled with their sensitivity to temperature, environment, and processing, dictate an integrated approach to design. The Advanced Composites Design Guide (DOD and NASA, 1973) recommends a close rapport among designer, toolmaker, and processor. To this liaison we would add the materials specialist and structural mechanician (Waddoups, 1968). This range of skills is needed to deal with the peculiarities of composites in structural applications. With this idea of an integrated approach in mind, we can now assess the status of each design activity individually.

STRUCTURAL MECHANICS

Structural analysis is the tool that permits a designer to specify a lamination sequence and part geometry that can be expected to meet design requirements. Governing equations and assumptions are the same as used for classical boundary value problems except that the constitutive relations will be anisotropic. Also, the solution must be more detailed than for isotropic cases because stresses other than principal values may exceed design allowables. A second reason for more detail is that safety margins in metals and polymers are usually based on yield, rather than on ultimates as in composites, which results in built-in conservatism in the form of stress redistribtion by plastic flow. On the plus side, the field of composite structural mechanics has been heavily studied during the last 15 years, resulting in the solution of numerous boundary value problems both analytically and by powerful finite difference and finite element techniques (Purdy, 1975). These analyses, termed macromechanics to distinguish them from the micromechanics of the previous chapter, usually assume the unidirectional ply to be homogeneous anisotropic continuum.

Linear Elastic Deformations

This is by far the best-developed branch of composite materials mechanics. Techniques for treating anisotropic elastic solids were pioneered by Lekhnitskii (1968, 1963). The topic has been developed in detail for laminated structures in numerous books (Ambartsumyan, 1970; Ashton et al., 1969; Calcote, 1969; R. Jones, 1975; Vinson and Chou, 1975) and articles (Bert and Francis, 1974; Advanced Composites Design Guide, Volume 4, DOD and NASA, 1973; Tsai, 1966). One reason for the emphasis on linear elastic formulation is that composites loaded parallel to a fiber direction at moderate temperatures exhibit approximately linear elastic behavior up to the time of failure. The stress and strain fields for composites subjected to moderate mechanical, thermal, or moisture loading can be estimated quite accurately, provided ply properties are known. The ply tensors required include stiffness or compliance, thermal expansion coefficient, thermal conductivity, moisture swelling coefficient, and moisture diffusivity.

The basic method outlined in the references cited is that of classical lamination theory. This approach uses tensor transformations to rotate the ply tensor into the appropriate orientation for calculating laminate properties. A number of authors have demonstrated the need for a balanced and symmetric lay-up both to minimize normal-shear and bending-stretching coupling when the laminate is loaded, and to reduce warpage during fabrication. Analyses of common structural elements have been summarized for use by designers. One-dimensional structures such as beams, trusses, and columns have been treated by Knoell and Robinson (1975) and by Bert and Francis (1974). Plates are presented by Bert (1975a) and in the texts by Ashton et al. (1969) and Calcote (1969) and by Bert (1975b). Volume II of the _Advanced Composites Design Guide_ (DOD and NASA, 1973) also treats each of these. The analyses presented in these references are best developed for relatively thin laminates that fulfill the conditions for plane stress. A typical lay-up for many plate and shell structures is $[0_i/\pm\theta_j/90_k]_{ns}$, where the selection of i, j, k, and θ depends upon how the structure is loaded. To maintain balance and symmetry, the designer must specify a laminate that contains an integral multiple of such a laminate. This minimum permissible gage somewhat restricts design freedom. For thicker plates and shells, where through-thickness stresses and displacement cannot be neglected, plate and shell theories are not so well developed. Bert (1975a) recommended increased experimental work to define better the limits of thin-shell approximations.

Input properties for these analyses are scattered through the technical literature. Moduli for graphite-reinforced epoxy and boron-reinforced epoxy have been tabulated in Volume IV of the _Advanced Composites Design Guide_ (DOD and NASA, 1973), and for glass-reinforced resin systems in Lubin (1969) and MIL-HDBK-17A (DOD, 1971).

Stresses and strains in composites caused by moisture and temperature are more subtle than those induced mechanically: both gradient and absolute magnitude must be known because thermomechanical anisotropy can generate stress even in an equilibrated structure (Gerstle and Reuter, 1976; Tauchert, 1974). Data for thermal expansion and moisture swelling coefficients are unavailable for some materials. Thermal conductivities and moisture diffusivities are likewise incomplete for many composites. However, when data are available, it appears that classical lamination theory can be used to predict laminate performance from ply properties (Walrath and Adams, 1979).

Viscoelastic, Nonlinear, or Plastic Deformations

Although much composite mechanical response is linear elastic, certain environments can produce nonlinear or inelastic response. This is especially true for matrix-dominated deformations like interlaminar shear. Viscoelastic deformations may also occur in fiber-controlled deformations at elevated temperatures in Kevlar-reinforced resins. Of chief interest to designers are viscoelastic effects, especially those related to residual stresses present in a laminate following fabrication, and the creep or relaxation that may occur either at elevated temperatures or under sustained loading. Methods of viscoelastic modeling and stress analysis for composites are given by Halpin (1968) and Schapery (1968, 1974), respectively. Many of the techniques and solutions of linear-elastic analysis can be used, with appropriate modifications to linear-viscoelastic structures, provided the conditions of the correspondence principle are met (Schapery, 1968). Although viscoelastic response of polymeric matrix composites can be significant, even well below the glass transition temperature, analytical understanding is not complete, and data for some important materials are unavailable (Schapery, 1975). In particular, experimental investigation is needed to determine the limits of applicability for the linear-viscoelastic models commonly used. It would also be of considerable design value if results were presented as a function of temperature, normalized to laminate glass transition temperature.

Nonlinear-viscoelastic deformation is usually a matrix-controlled phenomenon. Schapery (1975) suggested that nonlinear viscoelasticity arises in part from microcracking. This is probably true for materials in which the filaments remain elastic. For Kevlar composites, Ericksen (1976) demonstrated nonlinear-viscoelastic-composite behavior for unidirectional specimens pulled longitudinally. Schapery (1975) noted that some nonlinear constitutive relations exist, but that the field is not sufficiently developed, either analytically or experimentlly, for practical engineering design use.

Nonlinear-elastic or time-independent plastic deformations are seen in many composites strained beyond a certain value. Adams (1974) reviewed the field and presented anisotropic constitutive relations for use in formulating boundary value problems. Incremental analysis techniques may be used to solve certain problems, but the field is not well developed for resin matrix composites. More work, both analytical and experimental, is necessary if this area is to become useful to the designer.

Static Strength and Fracture

With knowledge of the stress state in the structure, the designer may assess the possibility that the struture will fail. Failure analysis requires the existence of usable criteria that quantitatively predict failure in a laminate. In this and the following two sections the status of failure analysis of composite structures is assessed. In this section we will consider the simplest case: time-independent, or quasi-static, room temperature strengths of laminates monotonically loaded to failure in either simple or multiaxial stress states. We will also consider the important design question of stress concentrations caused by material or geometric discontinuities. The problems of cyclic fatigue strength and of synergistic degradation by time, temperature, and moisture will be addressed in the two subsequent sections.

In the previous two sections we saw that lamina properties, if available, could be used to estimate laminate thermomechanical response. In contrast, laminate failure is not easily predicted from ply strengths. The first reason for this is the variety of failure modes that a laminate may exhibit, most of which are not catastrophic. A second reason is that a major assumption of lamination theory, the homogeneous anisotropic ply, is not satisfied in the fracture process. A third reason is that many composites exhibit radically different strengths in tension and compression. Kevlar composites, for example, are 5 to 8 times stronger in tension than in compression.

A number of review articles have treated various aspects of failure analysis. Rosen et al. (1975) state that knowledge of unidirectional ply strengths is a necessary, but probably not a sufficient condition for predicting laminate strengths. The authors note that other failure modes, such as those caused by interlaminar shear and normal stresses, are possible in laminates and that the problem is compounded by the multiplicity of fiber and matrix combinations, lamination sequences, and weave configurations, and is further confused by fiber anisotropy, matrix inelastic behavior, and statistical fiber strength. This leads to the conclusion that it is intrinsically difficult to generalize about laminate strength, each material having a somewhat unique response to a particular stress state.

Most previous lamina failure criteria have employed a macroscopic approach based on maximum stress, maximum strain, or a tensor polynomial. Wu (1974) reviewed the development of phenomenological lamina failure criteria and showed that for lamina strengths the tensor polynomial gives the best fit. Tsai and Hahn (1975) and Rowlands (1975), however, in reviewing laminate criteria found that no phenomenological approach is clearly superior to the others. The basic problem seems to be that, lacking a solid physical basis, each criterion can be judged only on its correlation to failure data, data that are expensive to obtain and that usually contain a fair amount of scatter (Guess and Gerstle, 1977).

The lack of a completely general laminate criterion means that in practice the designer can choose the simplest approach for which data are available. Vicario and Toland (1975) presented techniques based on limit or ultimate strengths and provided several numerical examples. They demonstrated the use of a laminate interaction diagram to determine the sequence of ply failure. This useful technique, also developed by Reed (1970) and Guess (1980), aids in setting safety margins for all plies in the structure. Transverse normal, intralaminar shear, and interlaminar shear failures are usually not catastrophic and appear to be a mechanism for reducing stress concentrations in the laminate (Rosen et al., 1975). However they do cause a loss in stiffness and may reduce fatigue strength and environmental resistance (Tsai and Hahn, 1975). Lamination sequences that reduce interply stresses are discussed by Pagano and Pipes (1971, 1973) and by Daniel et al. (1974). The problem of deterministic versus probabilistic strengths for design use is discussed in detail by B. Jones (1975). Although much information is available (e.g., <u>Advanced</u>

Composite Design Guide, Volume IV, DOD and NASA, 1973), the lack of basic mechanistic understanding and of a generally valid failure criterion hampers composite design.

Dealing with cutouts, fasteners, manufacturing flaws, and other stress risers brings up the subject of composite fracture mechanics, or more specifically, how to estimate the notch or crack sensitivity of a laminate. Both Ashton (1970) and Waddoups (1968) stated that little substantive work in fracture mechanics of composites from a design viewpoint had been done. Design information is contained in the Advanced Composites Design Guide, Volume II (DOD and NASA, 1973), and in Grimes and Greimann (1975). Smith (1975) reviewed the field and concluded that many of the basic linear-elastic fracture mechanics assumption are violated in composites. Composite fracture toughness values have been found to be specimen dependent, and plate ultimate strengths are a function of flaw size (Tsai and Hahn, 1975; Whitney, 1975; Whitney and Nuismer, 1974). The lack of certainty about what constitutes a critical flaw in a composite is a major impediment to composite design. Fracture models should be developed that account for composite inhomogeneity and inelasticity. These should include the role of the interface and the statistical nature of fiber strengths.

Fatigue Strength

In this section we will assess the time- and temperature-independent strength of composites subjected to cyclic loading. As was the case with static strengths, there is no simple criterion relating ply to laminate fatigue strength. Considerable tension-tension fatigue data exist for unidirectional ply structural composites (Ashton, 1970; Advanced Composites Design Guide, Volume IV, DOD and NASA, 1973; DuPont, 1978; Owen, 1975). With the exception of glass, all the high-performance reinforcements exhibit excellent resistance to this fatigue mode, i.e., the slope of their S-N curves (applied stress versus log cycles to failure) are small. Unidirectional plies of boron, graphite, and Kevlar are much less resistant to shear or compressive fatigue. Because pure uniaxial tension is very rare in practice, these latter modes tend to dominate in actual structures. For laminates the compressive and shear performance is improved by the presence of filaments in several directions. However, for equivalent tensile and compressive cycling, fatigue failure will likely occur in a compression or shear mode. (Ashton, 1970; Advanced Composites Design Guide, Volume IV, DOD and NASA, 1973; Owen, 1975). Data are not available for all composite laminates of interest.

Understanding of the fatigue process in composites is not complete. This is particularly true for compression and shear modes because these involve different damage mechanisms than are encountered for tensile fatigue in either composites or metals (Kunz and Beaumont, 1975). Owen (1975) noted that untreated graphite fibers were consistently inferior to treated material in these modes; he attributed the difference to reduced microbuckling of the treated fibers. Schapery (1975) added that the low thermal conductivity and dissipation mechanisms of polymeric matrix composites may influence crack-tip temperature and should be accounted for in any basic study.

The wearout model proposed by Halpin et al. (1973) is useful for design purposes. More sophistication could be built into such models to account for compression or shear failures (Rosen et al., 1975). Models to predict material response to varying amplitudes have not been developed for composites.

Fatigue failures often occur at joints and other discontinuities. In fact, MIL-HDBK-17A (DOD, 1971) gives fatigue data on glass composites only for jointed specimens. A mechanistic explanation of the effect of stress concentrations on fatigue should probably not be attempted until the uniform stress condition is better understood. One observation that stems from this is that tougher, more ductile matrices may be desirable to reduce composite notch sensitivity and increase fatigue strength (Drucker, 1975). More work is needed on this interesting problem.

Time-, Temperature-, and Moisture-Dependent Failure

The effect of time and environment on a stressed structure is not fully understood for either metals or composites. The situation is more acute for composites because resin matrices exhibit time and temperature-dependent deformation and failure, and are usually quite hygroscopic. Also, several common filaments (glass, Kevlar, and, probably, graphite) are known to have time-dependent strengths (Lifshitz, 1974; Toland and Chiao, 1978).

The response of a composite to a sustained load at constant temperature and humidity (creep rupture or static fatigue) is dependent upon both filament and matrix behavior. Lifshitz (1974) has shown that creep rupture for glass composites in tension is accelerated by the use of a more viscoelastic matrix. Creep rupture of glass composites has been explained by slow crack growth and hydroxyl attack (Wiederhorn, 1972). The mechanism of creep rupture in Kevlar is not yet understood (Chiao and Chiao, 1977; Konopasek and Hearle, 1977). Because nearly all available data have been gathered on unidirectional specimens in simple tension, and because no relationship exists for converting ply to laminate response, these data serve only as a qualitative guide to the designer. There is need for more data and improved material modeling and understanding. More information on this problem is contained in Chapter VII, entitled "Predictive Life Tests and Accelerated Testing."

Considerably more data are available on the effect of temperature and moisture on properties. Epoxy neat resin response is covered in detail by Morgan and O'Neal (1978). Extensive characterization has been done on boron-reinforced and graphite-reinforced epoxy systems (Browning, 1972; Browning et al., 1977; Heller et al., 1975; Hertz, 1971, 1972; IITRI, 1975; Mazor et al., 1978; Springer, 1978). In general these studies showed that fiber-dominated strengths were not greatly affected but that matrix-dominated properties such as shear, compressive, and transverse tensile strengths were considerably reduced by matrix softening. The situation is somewhat different for Kevlar composites, because the fiber is also hygroscopic and has a softening temperature little above that of the matrix. Allred (1980a, 1980b) has shown that the flexural strength of Kevlar is reduced by the synergistic effect of both moisture and temperature on both fiber and matrix. Such synergism is seen in other structural composites as well, but the effect is confined primarily to the matrix.

The time, temperature, and moisture data that exist are scattered through the literature and need to be compiled in handbooks for design purposes, and related, preferably, to glass transition temperature. The third edition of the Advanced Composites Design Guide (DOD and NASA, 1973) does not contain data in this important area. We recommend that the fourth edition, now in preparation, rectify this. Also needed are improved material models and corroborative testing techniques for laminates.

FABRICATION

The differences between metal and composite structural design are especially evident in the fabrication process. The most obvious difference is that all of the required mechanical properties in a composite structure are developed as the part is being made. This places a responsibility on the designer to interact closely with the process engineer and to become knowledgeable about the various fabrication techniques described in Chapter IV. Such knowledge, especially about the limitations of each technique, can prevent many potential problems from ever leaving the drawing board (Advanced Composites Design Guide, Volume 1, DOD and NASA, 1973).

Most of the current fabrication techniques for composites were originally developed for glass fibers. Design information is summarized by Welhart (1977), and covered more thoroughly in MIL-HDBK-17A (DOD, 1971), and in Chapters 13 to 15, and 17 to 20 in Lubin (1969). Specifics for processing and machining graphite and boron structural members are given in Volume III of the Advanced Composites Design Guide (DOD and NASA, 1973) and are given for Kevlar in the Kevlar 49 Aramid Data Manual (Dupont, 1974 ff). The techniques and practices described in these references are capable of producing good quality, thin (7-mm [0.28-in.]) laminates with polyester, epoxy, or phenolic matrices that require cure temperatures up to 200°C (392°F). Thicker sections, complicated geometries, or tight tolerances usually require a trial-and-error approach. This is because the composite processing field lacks the basic understanding and material modeling needed to predict resin kinetics and rheology during fabrication. The resulting inconsistent properties on nonstandard parts demonstrate the need for basic material understanding on which to base processing specifications for thick or complicated sections and for cures above 200°C (392°F).

Besides the obvious difference between metal and composite fabrication, composite processing lacks some of the sophistication that permits a designer to extract maximum performance from a metal. For example, a metal part may be specified with a variety of heat treatments or surface hardnesses to aid its resistance to a particular service environment. Innovative work on such things as residual stress control, matrix selection, void reduction, and surface finish techniques could produce stronger, more consistent laminates.

CERTIFICATION

The designer needs unambiguous inspection and test techniques to guarantee that the structure is made to specifications. Volume III of the Advanced Composites Design Guide (DOD and NASA, 1973) lists some 21 possible problem areas that may occur in a composite skin honeycomb structure. Available inspection techniques include analytical inspection of constituents (Chapter II) cure inspection (Chapters III and IV), coupon testing (Chapter V), nondestructive evaluation (Chapter VIII), and testing of the completed laminate or structure. As was the case with fabrication, a designer should become familiar with the limitations of these methods, and, if possible, modify the design to relax or eliminate specifications that are difficult to guarantee. Because these inspection and quality assurance techniques are addressed in other chapters, they will not be reassessed here.

In this section we will comment on several problems of certification commonly faced by the composite structural designer. First, because of concerns about safety, designers have placed very stringent specifications on raw materials and processing conditions for primary structures (Advanced Composites Design Guide, Volume III, DOD and NASA, 1973). It would be useful and cost effective if information were available as to what degree these specifications could be relaxed and still guarantee an acceptable structure. Second, glass transition temperature is a basic resin property that is indicative of its degree of cure and usable temperature range. The glass transition temperature is not used to the same extent in predicting behavior for composites as in neat resins. Third, common nondestructive evaluation techniques will detect very small flaws in laminates. Because laminate flaw sensitivity is not established, the information cannot be used to predict the reduction in safety margin resulting from a particular flaw.

Certification usually raises the question of proof testing, which in metal structures is a means of proving that a structure contains no flaw greater than a certain acceptable size. Rosen et al. (1975) seriously question the use of proof testing because of the multiplicity of failure mechanisms in a composite and the lack of correlation between static and fatigue strengths. They argue that damage done during proof testing may be a different kind, and possibly more severe, than that which the structure encounters in service.

The last topic in certification is that of predicting the remaining life of a part in service. This requires a technique to detect and assess the criticality of flaw growth in the structure. At present there is no such method available to the designer. One method for Kevlar- and glass-reinforced composites that has been tried and found wanting is that of strength retention, i.e., residual strength following some period of time on load (Chiao, 1978). An assessment of long-term failure prediction is provided in Chapter VIII.

CONCLUSIONS

Structural Mechanics

1. Linear-elastic deformations, including hygrothermal effects, can be predicted accurately from ply properties using classical lamination theory. A substantial ply and laminate mechanical data base exists.

2. Nonlinear-viscoelastic or plastic laminate behavior can be predicted in some materials, in simple stress states, using linear-viscoelastic or incremental analysis techniques. Viscoelastic data on many important composites are scarce.

3. There exists no criterion for assessing the reduction of properties resulting from an arbitrary flaw in a structure.

4. Proof testing of composite structures is a questionable practice.

Fabrication

1. Fabrication techniques for producing thin laminates in simple geometries with moderate cure cycles are well developed.

2. Thick sections, complicated geometries or lay-ups, tight tolerances, or very-high-temperature cures can only be approached through a trial-and-error process.

Certification

1. Available analytical inspection and nondestructive evaluation technologies are adequate to determine whether a part has been

made to specification. It is not currently known, however, what constitutes an acceptable deviation from the specification.

2. The synergistic effect of temperature and time on loaded structures needs more fundamental study. This includes mechanisms, modeling, and testing.

RECOMMENDATIONS

For composites to be used routinely in structures, the designer needs considerable information, much of which is either unavailable or scattered throughout the literature. Our general recommendation is for the continued expansion, updating, and promulgation of design-oriented handbooks like the Advance Composites Design Guide, published by DOD and NASA. These handbooks should include detailed material specifications and design allowables. Our specific recommendations follow.

Structural Mechanics

1. The areas of nonlinear-elastic, viscoelastic, inelastic, and hygrothermal laminate response should be experimentally investigated to determine and extend the limits of current theory.

2. Laminate failure data and models under combined stresses are needed for a range of materials and lay-ups. These should include both sequence and mode of failure.

3. Models that account for inhomogeneity and inelastic matrix deformation should be formulated to assess flaw criticality in a laminate. These models should be verified experimentally.

4. Cyclic fatigue and creep rupture of laminates should be studied with the goal of determining the mechanism of crack nucleation and growth.

5. The use of tougher, more ductile matrices as a means of reducing laminate notch sensitivity and increasing fatigue strength should be investigated.

6. No generally valid techniques exist that adequately predict laminate static strengths from ply strengths. Phenomenological failure envelopes do not predict the lamina failure sequence or mode.

7. Classical linear-elastic fracture mechanics cannot predict laminate sensitivity to a flaw.

8. Engineering data on laminate fatigue strength have been gathered, but understanding is incomplete, especially for compression and combined tension-compression loading.

9. Creep strength for certain composites is not well understood; laminate data are very scarce, and predictive techniques have not been developed.

10. Ply strength as a function of temperature and moisture is available for most composites. Laminate data are available for some materials; predictive techniques are lacking.

Fabrication

1. Processing specifications suitable for a range of laminate thicknesses, geometries, cure temperatures, and applications should be developed. These will require knowledge of resin kinetics and rheology of the laminate.

2. Residual stress control, void reduction and surface treatments, and other process-controlled phenomena should be studied with the goal of tailoring final properties for maximum material performance.

Certification

1. Methods should be developed to assess the severity of deviations from design specifications. Unrealistic and expensive specifications should be relaxed wherever possible.

2. The proof test should be reexamined; it should only be adopted as a design tool for valid theoretical and experimental reasons.

3. Techniques to predict the useful life of a structure, based on an understanding of the fracture process, are needed.

REFERENCES

Adams, D. F., "Elastoplastic Behavior of Composites," Composite Materials, Vol. 2, Mechanics of Composite Materials, G. P. Sendeckyj, ed., Academic Press, Inc., New York, 1974, pp. 169-208.

Allred, R. E., "The Effect of Temperature and Moisture Content on the Flexural Response of Kevlar/Epoxy Laminates: Part I[0/90] Filament Orientation," Preprint, Sandia National Laboratories, Submitted to Journal of Composite Materials, 1980a.

Allred, R. E., "The Effect of Temperature and Moisture Content on the Flexural Response of Kevlar/Epoxy Laminates: Part II [±45, 0/90] Filament Orientation," Preprint, Sandia National Laboratories, Submitted for publication to Journal of Composite Materials, 1980b.

Ambartsumyen, S. A., The Theory of Anisotropic Plates, translated from Russian, Technomic Publishing Co., Westport, Conn., 1970.

Ashton, J. E., "Implications of the Behavior of Advanced Composite Materials," J. Franklin. Inst., 290, 549-566 (1970).

Ashton, J. E., J. C. Halpin, and P. H. Pettit, Primer on Composite Materials: Analysis, Technomic Publishing Co., Westport, Conn., 1969.

Bert, C. W., "Analysis of Plates," Composite Materials, Volume 7, Structural Design and Analysis, Part I., C. C. Chamis, ed., Academic Press, Inc., New York, 1975a, pp. 149-206.

Bert, C. W., "Analysis of Shells," Composite Materials, Vol. 7, Structural Design and Analysis, Part I, C. C. Chamis, ed., Academic Press, Inc., 1975b, pp. 207-258.

Bert, C. W., and P. H. Francis, "Composite Material Mechanics: Structural Mechanics," AIAA J., 12(9), 1173-1186 (1974).

Browning, C. E., The Effects of Moisture on the Properties of High Performance Structural Resins and Composites, AFML-TR-72-94, Air Force Materials Laboratory, 1972.

Browning, C. E., G. E. Husman, and J. M. Whitney, "Moisture Effects in Epoxy Matrix Composites," Composite Materials: Testing and Design, ASTM STP 617, Fourth Conference, Philadelphia, 1977, pp. 481-496.

Calcote, L. R., The Analysis of Laminated Composite Structures, Van Nostrand Reinhold Co., New York, 1969.

Chiao, T. T., Some Interesting Mechanical Behaviors of Fiber Composite Materials, Preprint UCRL-80908, Rev. 1, Lawrence Livermore Laboratory, Livermore, Calif., June, 1978.

Chiao, C. C., and T. T. Chiao, *Aramid Fibers and Composites*, Preprint UCRL-80400, Lawrence Livermore Laboratory, Livermore, Calif., December, 1977.

Daniel, I. M., R. E. Rowlands, and J. B. Whiteside, "Effects of Material and Stacking Sequence on Behavior of Composite Plates with Holes," *Exper. Mech.*, *14*, 1-9 (1974).

Department of Defense (DOD), "Reinforced Plastics," Part I of *Plastics for Aerospace Vehicles*, MIL-HDBK-17A, Washington, D.C., 1971.

DOD and NASA, *Advanced Composite Design Guide*, Vols. 1 to 4, third edition, Advanced Development Division, Air Force Materials Laboratory, Wright-Patterson AFB, 1973.

Drucker, D. C., "Yielding, Flow and Failure," *Inelastic Behavior of Composite Materials*, Vol. 13, American Society of Mechanical Engineers, New York City, 1975, pp. 1-15.

E. I. DuPont de Nemours & Co., Inc., Wilmington, Dela., Textile Fibers Department, *Kevlar 49 Aramid Data Manual*, 1974ff.

E. I. DuPont de Nemours & Co., Inc., Wilmington, Dela., "Characteristics and Uses of Kevlar 49 Aramid High Modulus Organic Fiber, " Bulletin K-2, February, 1978.

Ericksen, R. H., "Room Temperature Creep of Kevlar 49/Epoxy Composites," *Composites*, *7*(3), 189-194 (1976).

Gerstle, F. P., Jr., and R. C. Reute, Jr., "Thermal Stress Behavior in Cylindrically Orthotropic Structures," *Failure Modes in Composites III*, 105th AIME Annual Meeting, Las Vegas, Feb. 22-26, 1976, pp. 239-259.

Grimes, G. C., and L. F. Greimann, "Analysis of Discontinuities, Edge Effects, and Joints," *Composite Materials*, Vol. 8, *Structural Design and Analysis*, Part II, C. C. Chamis, ed., Academic Press, Inc., 1975, pp. 135-230.

Guess, T. R., "Biaxial Testing of Composite Cylinders: Experimental-Theoretical Comparison," *Composites*, *11*(3) 139 (1980).

Guess, T. R., and F. P. Gerstle, Jr., "Deformation and Fracture of Resin Matrix Composites in Combined Stress States," *J. Compos. Mater.*, *11*, 146-163 (1977).

Halpin, J. C., "Introduction to Viscoelasticity," *Composite Materials Workshop*, S. W. Tsai, J. C. Halpin, and N. J. Pagano, eds., Technomic Publishing Co., Westport, Conn., 1968, pp. 87-152.

Halpin, J. C., K.L. Jerina, and T. A. Johnson, "Characterization of Composites for the Purpose of Reliability Evaluation," *Analysis of Test Methods for High Modulus Fiber and Composites*, ASTM STP 521, Philadelphia, 1973, pp. 5-64.

Heller, R. A., H. F. Brinson, and A. B. Thakker, "Environmental Effects on Fiber Reinforced Composites," *Polymer Engineering and Science*, *15*(11), 781-788 (1975).

Hertz, J., "High Temperature Strength Degradation of Advanced Composites," Space Shuttle Materials, *National SAMPE Technical Conference*, Huntsville, Ala., October 5-7, 1971, pp. 9-16.
Hertz, J., "Moisture Effects on the High Temperature Strength of Fiber-Reinforced Resin Composites," *4th National SAMPE Technical Conference*, Palo Alto, Calif., October 17-19, 1972, pp. 1-7.

Illinois Intitute of Technology Research Institute (IITRI), *Development of Engineering Data on the Mechanical and Physical Properties of Advanced Composite Materials*, AFML-TR-74-266, February, 1975.

Jones, B. H., "Probabilistic Design and Reliability," *Composite Materials*, Vol. 8, *Structural Design and Analysis*, Part II, C. C. Chamis, ed., Academic Press, Inc., New York, 1975, pp. 34-72.

Jones, R. M., Mechanics of Composite Materials, Scripta Publishing Co., Washington, D.C., 1975.

Knoell, A. C. and E. Y. Robinson, "Analysis of Truss, Beam, Frame, and Membrane Components," *Composite Materials*, Vol. 7, *Structural Design and Analysis*, Part I, C. C. Chamis, ed., Academic Press, Inc., New York, 1975, pp. 99-148.

Konopasek, L., and J. W. S. Hearl, "The Tensile Fatigue Behavior of Para Oriented Aramid Fibers and Their Fracture Morphology," *J. Appl. Polym. Sci.*, *21*, 2791-2815 (1977).

Kunz, S. C., and P. W. R. Beaumont, "Microcrack Growth in Graphite Fiber-Epoxy Resin Systems During Compressive Fatigue," *Fatigue of Composite Materials*, ASTM STP 569, American Society for Testing and Materials, Philadelphia, 1975, pp. 71-91.

Lekhnitskii, S. G., *Theory of Elasticity of an Anisotropic Body*, P. Fern, trans., Holden Day, Inc., San Francisco, 1963.

Lekhnitskii, S. G., *Anisotropic Plates*, S. W. Tsai and T. Cheron, trans., Gordon and Breach Science Publishers, Inc., New York, 1968.

Lifshitz, J. M., "Time-Dependent Fracture of Fibrous Composites," *Composite Materials*, Vol. 5, *Fracture and Fatigue*, L. J. Broutman, ed., Academic Press, Inc., 1974, pp. 249-311.

Lubin, G., *Handbook of Fiberglass and Advanced Plastics Composites*, Van Nostrand Reinhold Co., New York, 1969.

Mazor, A., L. J. Broutman, and B. H. Eckstein, "Effect of Long-Term Water Exposure on Propertries of Carbon and Graphite Fiber Reinforced Epoxies," *Polym. Eng. Sci.*, *18*(5), 341-349 (1978).

Morgan, R. J., and J. E. O'Neal, "The Durability of Epoxies," *Polym. Plast. Technol. Eng.*, *10*(1), 49-116 (1978).

Owen, M. J., "Fatigue of Carbon-Fiber-Reinforced Plastics," *Composite Materials*, Vol. 5, *Fracture and Fatigue*, L. J. Broutman, ed., Academic Press, Inc., New York, 1975, pp. 341-369.

Pagano, N. J., and R. B. Pipes, "The Influence of Stacking Sequence on Laminate Strength," *J. Comp. Mater.*, *5*, 50-57 (1971).

Pagano, N. J., and R. B. Pipes, "Some Observations on the Interlaminar Strength of Composite Laminates," *Int. J. Mech. Sci.*, *15*, 679-688 (1973).

Purdy, D. W., "Discrete Element Analysis of Composite Structures," *Composite Materials*, Vol. 8, *Structural Design and Analysis*, Part II, C. C. Chamis, ed., Academic Press, Inc., New York, 1975, pp. 1-3.

Reed, D. L., "Point Stress Laminate Analysis," General Dynamics Corp., Fort Worth Division, Rept. FZM-5494, April, 1970.

Rosen, B. W., S. V. Kulkarni, and P. V. McLaughlin, Jr., "Failure and Fatigue Mechanisms in Composite Materials," *Inelastic Behavior of Composite Materials*, Vol. 13, American Society of Mechanical Engineers, New York City, 1975, pp. 17-72.

Rowlands, R. E., "Flow and Failure of Biaxially Loaded Composites: Experimental-Theoretical Correlation," *Inelastic Behavior of Composite Materials*, Vol. 13, American Society of Mechanical Engineers, New York City, 1975, pp. 97-125.

Scala, E., *Composite Materials for Combined Functions*, Hayden Book Co., Inc., Rochelle Park, N.J., 1973.

Schapery, R. A., "Stress Analysis of Viscoelastic Composite Materials," *Composite Materials Workshop*, S. W. Tsai, J. C. Halpin, and N. J. Pagano, eds., Technomic Publishing Co., Westport, Conn., 1968, pp. 153-192.

Schapery, R. A., "Viscoelastic Behavior and Analysis of Composite Materials," *Composite Materials*, Vol. 2, *Mechanics of Composite Materials*, G. P. Sendenckyj, ed., Academic Press, Inc., New York, 1974, pp. 85-168.

Schapery, R. A., "Deformation and Failure Analysis of Viscoelastic Composite Materials," *Inelastic Behavior of Composite Materials*, C. T. Herakovich, ed., Vol. 13, American Society of Mechanical Engineers, New York City, 1975, pp. 127-155.

Smith, C. W., "Limitations of Fracture Mechanics as Applied to Composites," *Inelastic Behavior of Composite Materials*, Vol. 13, American Society of Mechanical Engineers, New York City, 1975, pp. 157-175.

Springer, G. S., "Environmental Effects on Epoxy Matrix Composites," Composite Materials: Testing and Design (Fifth Conference), New Orleans, ASTM STP 674, S. W. Tsai, ed., American Society for Testing and Materials, Philadelphia, 1979, pp. 291-312.

Tauchert, T. R., "Thermal Stresses in an Orthotropic Cylinder Subject to a Radial Steady State Temperature Field," *Proceedings of the Seventh Southeastern Conference on Theoretical and Applied Mechanics*, Washington, D.C., March, 1974, pp. 1-11.

Toland, R. H., and T. T. Chiao, *Stress Rupture Life of Kevlar/Epoxy Spherical Pressure Vessels*, Part 2, Report UCID-17755, Lawrence Livermore Laboratory, Livermore, Calif., June 30, 1978.

Tsai, S. W., "Theoretical Aspects," Part II of *Mechanics of Composite Materials*, AFML-TR-66-149, Air Force Materials Laboratory, 1966.

Tsai, S. W., and H. T. Hahn, "Failure Analysis of Composite Materials," *Inelastic Behavior of Composite Materials*, Vol. 13, American Society of Mechanical Engineers, New York City, 1975, pp. 73-96.

Vicario, A. A., and R. H. Toland, "Failure Criteria and Failure Analysis of Composite Structural Components," *Composite Materials*, Vol. 7, *Structural Design and Analysis*, Part I, C. C. Chamis, ed., Academic Press, Inc., New York, 1975, pp. 52-97.

Vinson, J. R., and T. W. Chou, *Composite Materials and Their Use in Structures*, Applied Science Publishers, Essex, England, 1975.

Waddoups, M. E., "Characterization and Design of Composite Materials," *Composite Materials Workshop*, S. W. Tsai, J. C. Halpin, and N. J. Pagano, eds., Technomic Publishing Co., Westport, Conn., 1968, pp. 254-308.

Walrath, D. E., and D. F. Adams, "Moisture Absorption Analysis of a Thematic Mapper Graphite/Epoxy Composite Structure," *Modern Developments in Composite Materials and Structures*, J. R. Vinson, ed., American Society of Mechanical Engineers, December, 1979.

Welhart, E. K., "How To Fabricate Advanced Composites," *Mater. Eng.*, No. 8, 50-53 (1977).

Whitney, J. M., "The Effect of Stress Concentrations on the Fracture Behavior of Fiber Reinforced Composite Materials," *Proceedings of the 12th Annual Meeting of the Society of Engineering Science*, Austin, Tex., October 20-22, 1975, pp. 173-179.

Whitney, J. M., and R. J. Nuismer, "Stress Fracture Criteria for Laminated Composites Containing Stress Concentrations," *J. Compos. Mater.* *8*, 253-265 (1974).

Wiederhorn, S. M., "A Chemical Interpretation of Static Fatigue," *J. Amer. Ceram. Soc.* *55*(2), 81-85 (1972).

Wu, E. M., "Phenomenological Anisotropic Failure Criterion," *Composite Materials*, Vol. 2, *Mechanics of Composite Materials*, G. P. Sendeckyj, ed., Academic Press, Inc., New York, 1974, pp. 353-4.

CHAPTER VII

PREDICTIVE LIFE TESTS AND ACCELERATED TESTING

Predictive life tests at accelerated time scales require a knowledge of material behavior that transcends traditional materials characterization. It is the objective of this chapter to describe in synoptic form the state of the art of predictive life and accelerated characterization techniques for polymeric composites and to point out areas of needed research.

One of the key elements in the failure analysis and certification of a structural composite--as in any structure--is an estimate of its life under service conditions. Predictive life tests and techniques for accelerating degradation and failure are therefore central to quality assurance and reproducibility in composite structures. The goal of any predictive life or accelerated testing is to ensure that the structure not fail in service i.e., that it be reliable. Reliability may be defined (Kapur and Lamberson, 1977; Magistad, 1981) as the probability that a structure will perform as intended under design conditions for a specified period. Reliability may also be thought of as a measure of the effects of design, production, inspection, and environment on the service life of the structure. Both definitions convey the statistical nature of reliability, and indicate the need to include some discussion of the statistical distribution of composite properties. The sources of and methods for detecting property variations have been treated in other chapters. In this chapter variability as it affects life testing will be discussed. Then accelerated testing and the conditions under which it is valid will be considered. In each discussion, recommendations for fruitful areas of research will be given. Throughout the chapter, the aim is to demonstrate the need for good experimental design and material modeling, and the importance of knowledge of the basic mechanisms of degradation.

BACKGROUND -- GENERAL OBSERVATIONS

Before assessing life and accelerated testing in composites, it is useful to review certain problems and precepts common to all such testing. This is not meant to serve as a manual on long-term testing; however, in reading the composites literature in this area, indications were seen that not every researcher is aware of these points.

The first problem confronting life or aging tests is identification of the stresses, and their distributions to which the structure will be subjected. Here, stress is used in the general sense: applied load, temperature, moisture, residual cure stress, radiation, oxidation, freeze-thaw, corrosive agents, etc., and their respective magnitude, frequency, and time dependence (Lipson and Sheth, 1972; Magistad, 1981).

The next essential feature is the definition of failure mode or modes (Gillen and Mead, 1980; Martin Company, 1962). Structural failure is usually defined either as excessive deformation (e.g., creep or buckling) or as fracture. Deformational failures depend upon stiffness or compliance properties. Although complicated in composites by material anisotropy, these properties and their stress-time dependence can usually be considered as homogeneous within a ply. In contrast, fracture is an heterogeneous phenomenon which depends upon local behavior of the material. Andrews (1968) defines six types of fracture for unreinforced polymers. For long-term reliability the most important types are cyclic fatigue, creep rupture or static fatigue, environmental stress cracking, and abrasion. In composites, each of these types must be further subdivided because of anisotropy of strength and because many composites have very different strengths in tension and compression. Therefore, it is very important for the critical failure mode(s) to be identified early in the course of any life or aging study.

The third problem that must be addressed in life and accelerated testing is that of the mechanism that causes failure. A detailed understanding of the physics and chemistry of the failure mechanism is not always possible, and is probably warranted only in critical structural elements. However, unless some understanding of the failure mechanism is attained, there can be no rational method for constructing a predictive model for accelerating failure. This is a very important and difficult step, since the controlling mechanism may change with time.

The design of life and aging experiments requires a combination of care and boldness. Care is needed to prevent the wasting of valuable specimens and time on inconclusive results. Boldness is needed to screen out unimportant stresses early in the program. To reach these goals, long-term experiments require a systems approach (Hufferd, 1980; Magistad, 1981) and should be based on a sound statistical approach incorporating orthogonal data structures and randomized data sequences (Dupont, 1975). Besides eliminating unimportant effects, such an approach will help identify the presence of any synergism between stresses.

Having defined stresses and failure modes, the next task for the researcher is selection of a suitable test specimen. The goal is to select the smallest element representative of the actual structure that will fail in the mode of interest. The advantages of small specimens are cost, control, and the possibility of testing more specimens per environmental chamber. However, since composite strengths do depend on size (Zweben, 1970) and exhibit edge effects (Pagano and Pipes, 1971), care is needed.

To complete these observations, it is useful to try to contrast composites with structural alloys. The first major difference is the variety of failure modes brought on by anisotropy and different tension -compression behavior. Metals either yield or crack. Composite failure in most stress states is a complex process, and is usually described in terms of damage accumulation, rather than in terms of a reasonably well-defined plastic zone or crack propagation as in metals. The second major difference is that during the last 15 years reinforcing fibers with dramatically increased strength and stiffness have been developed and introduced. The comparable growth in metal properties occurred over a much longer period. Consequently the composite researcher, looking for fundamental failure mechanisms on well characterized materials, was faced with a very fluid situation caused by rapidly changing fiber properties. These increases have caused substantial problems for scientists engaged in long-term composite testing. However, the outlook has improved because the properties of fibers being marketed appear to have stabilized, both in magnitude and consistency during the past five years.

STATISTICS OF FAILURE

The inherent variability of materials strongly influences the design of structures. To design for safe life, it is necessary to consider minimum material strength or stiffness that might be realized in service. Because material strength and stiffness are statistical variables, they must be described in a nondeterministic manner. For example, contemporary designs of aircraft utilize allowable properties which insure minimum strength at a given confidence level (Jones, 1969, 1975). However, the anisotropic, heterogeneous nature of composite materials make this approach too simple. Weibull statistics (Weibull, 1939) have been used to adequately describe composite failure statistics, but since these materials exhibit multiple failure modes, no single statistical descriptor is adequate. Furthermore, traditional statistical descriptors are unable to discern the source or cause of variability. Hence, the potential reduction of variability by quality control is marked by the inherent variabilities of the constituents or other sources.

Structural failure is not always determined by materials strength properties. Compressive stress fields lead to structural instability which is governed by material stiffness. Jackson (1975) reported structural failure variablity less than the variabilities of the anisotropic material strength properties. This resulted because structural failure was governed by local material instability and hence stiffness properties that typically exhibit less variability than do strength properties.

Not only do composite materials exhibit multiple failure modes and hence require statistical descriptors for each, but material variability has been shown to be a function of stress and environmental history (Wu, 1975). For example, prestressing of the composite prior to polymerization has been shown to reduce composite strength variability and increase allowable strength by prebreaking fibers containing defects which are the source of low load failure (Mills, 1975).

The statistics of failure modes and phenomena in composite materials have been studied by many researchers (e.g., Wu, 1975), however, what is now needed is a comprehensive treatment that allows for multiple failure modes and processes and that models the sources of variability.

KINETIC MODELING

A number of phenomena that influence the life of a polymeric composite material are time dependent. Among these are diffusional processes, viscoelastic deformation, fatigue, chemical reactions, and a category that may be broadly classified as aging. The diffusional processes of primary interest are the absorption and desorption of solvents (primarily water) by the polymer and at the polymer and fiber interface. Viscoelastic deformation of the composite may be attributed primarily to that of the polymer phase. Chemical reactions that result in new cross-links are known to continue throughout the life of a thermosetting polymer. Finally, all other time-dependent phenomena are generally collected under the term "aging." Aging has been classified as physical, chemical, and mechanical aging (Hufferd, 1980).

The physical aging of amorphous polymers has been described in great detail in a publication by Struik (1978). The primary thesis of that work is that physical aging in amorphous polymers is caused by changes in free volume wherein the transport mobility of particles or molecules decreases with time. Changes in relaxation times are the primary effects of physical aging in polymers. It is further shown that physical aging is thermo-reversible when the polymer is heated above its glass transition temperature. Furthermore, the superposition of creep results for various degrees of aging shows that physical aging phenomenon is unchanged by time. In addition, all polymers are shown to exhibit similar aging phenomena. Finally, aging is shown to disappear at low temperatures but to continue for very long times at conditions at or above ambient.

The author describes several other processes similar to aging. Swelling and deswelling of glassy polymers produce changes in segmental mobility; therefore, the diffusivity of solvent molecules changes with time. It is expected that during swelling and deswelling the mechanical properties of the polymer will change in the same way as during free volume changes.

A second process similar to physical aging is cross-linking reactions or chemical aging. Cross-linking is accompanied by a decrease in segmental mobility of the polymer chains. Because the cross-linking phenomenon is produced as a result of the presence of unreacted species and is self-decaying, it will continue for a long time, thus changing the properties of the material continuously.

It is also shown that aging affects properties other than mechanical. For example, at temperatures near the glass transition temperature, the processes of dielectric and mechanical behavior are quite similar. In addition to dc polarization and dielectric loss as a function of frequency, aging will also influence dc conductivity.

Physical aging appears to produce insignificant changes in impact strength of polymers at temperatures below the ductile to brittle transition. However, for the ductile region, decreases in free volume associated with physical aging result in decreases in impact strength. In contrast to homopolymers, the impact strength of rubber-modified systems is not influenced by aging. This difference exists because modified polymers owe their ductility to a different mechanism.

The influence of mechanical deformations on aging results from the fact that the segmental motion produced generates free volume whether the deformations are tensile, compressive, or shearing modes. Hence, it should be expected that mechanical deformations would act to reverse the aging process.

Environments that promote aging include ultraviolet and gamma radiation, ozone, oxygen, solvent, temperature, moisture, and sustained load. To model these phenomena, it is necessary to develop rate models (e.g., the Arrhenius type). Perhaps the most serious problem in this regard is that the aging processes are not independent. It is well known that mechanical or thermal stress accelerates the aging processes because of the mechanisms just described (Hufferd, 1979). In addition, recent work has shown that the simultaneous action of cyclic temperatures increases the moisture saturation level of many polymeric composite systems (McKaugue et al., 1975). Hence, the required rate models must reflect the combined effects of adverse environmental parameters such that the synergism of multiple environmental conditions may be considered.

The degradation of material properties caused by cyclic mechanical and thermal stresses has been modeled by a deterministic power law model that presumes uniform degradation of the material with fatigue load history. This approach is termed the "wearout model" (Halpin, 1973). Unfortunately, the wearout model at its current stage of development ignores the existence of competing failure processes and, as such, is appropriate only when a single failure process dominates. This is certainly the case for interlaminar flaw growth where interlaminar defects grow in a self-similar manner along interlaminar planes. Efforts to model this process by classical fracture mechanics have been initiated, and early results indicate a high probability for the success of this method (Ramkumar et al., 1978). However, the important question of the criticality of interlaminar flaws is just beginning to be addressed. It would appear that large interlaminar damage can be sustained without loss of in-plane tensile strength or stiffness, but compressive and transverse shear properties are reduced.

ACCELERATED LIFE TEST METHODS

An accelerated life test method is a procedure based on sound engineering and statistical assumptions that uses statistical models and physical laws of failure to transform reliability information generated in a short time to the prediction of lifetime estimates, or reliability. Yurkovsky et al. (1967) evaluated a number of techniques and listed over 500 references.

To certify advanced composite materials for structural applications, it is necessary to develop methods that will allow testing to be accomplished in an accelerated time span while properly simulating the significant parameters. This problem has been and is continuing to be addressed for contemporary metallic materials. However, the polymeric nature of the matrix phase for advanced composite materials further complicates the problem. Fortunately, the time-temperature superposition principle (Ferry, 1961; Halpin, 1968; Shapery, 1968) is generally applicable for polymeric matrices. This principle allows long-term viscoelastic deformations to be determined in shorter times by raising the temperature of the polymer. The superposition principle should therefore provide the basic tool for accelerated testing of polymeric composites. Preliminary efforts that apply this principle in fatigue loading of composite materials are reported by Rotem and Nelson (1979). A recent study by Ho (1980) investigated the potential for developing equivalent thermal and moisture environments for long-term fatigue tests. Such an equivalence would allow accelerated tests that avoid the long times associated with moisture diffusion. The results to date are inconclusive.

Because the failure of composite materials is a complex phenomenon that occurs as multiple failure modes, it is important that accelerated test methods model each of the relevant failure processes. In this way, the combined processes of competing modes will be properly described.

Accelerated test methods for polymeric composites must account for aging of the polymeric phase and the interfacial bond between fiber and matrix. This problem has received very little attention. However, accelerated test methods require the development of a basic understanding of the aging process such that appropriate superposition principles can be developed. Hence, it is appropriate that efforts be undertaken to develop aging rate models sufficient to meet these needs.

CONCLUSIONS

1. The proper characterization of organic matrix composites includes determination of the behavior of the material over its anticipated or extended life. Because polymeric systems are subject to various rate processes that alter properties of these materials, it is necessary to develop methodology (including the development of rate models for the various phenomena that alter material properties or performance) that will allow for long-term characterization.

2. The models for statistics of failure of composite materials do not now model source of variability. Furthermore, no comprehensive treatment is available that allows for either multiple failure modes and processes, or synergism of processes.

3. The models of kinetic phenomena in composite materials are in an early stage of development. Models for the phenomena are modeled independently, yet interactions among diffusional, reaction, physical and mechanical phenomena are extremely important in determining life.

4. No coherent methodology has been developed for accelerated life testing of composite structures.

RECOMMENDATIONS

1. The most significant need in the field of prediction of the life of organic matrix composite structures is the development of synergistic rate models that account for the interaction of material deformation, damage, stress, and environmental parameters. A great deal of fundamental work is required in this area.

2. Kinetic models of polymeric aging resulting from temperature, stress, fatigue, and diffusion are required for these material systems. In particular,

   - physical aging models must be developed to describe spontaneous enthalpic relaxation-induced consolidation and embrittlement of the polymer, and

   - chemical rate and diffusional models of decomposition reactions caused by service environments are required.

3. Methodologies that produce accelerated degradation rates must be developed such that the structure can be tested to several lifetimes in a time frame less than real time.

4. Fatigue models that utilize accelerated load and environment spectra to evaluate structural life should be developed and validated.

5. Comprehensive models of material variability that account for multiple failure modes and model source of variability must be developed.

REFERENCES

Beaumont, P. W. R., P. G. Riewald, and C. Zweben, Methods for Improving the Impact Resistance of Composite Materials, ASTM STP 568, American Society for Testing and Materials, Philadelphia, 1975.

E. I. du Pont, Applied Technology Division, "Strategy of Experimentation," Revised Edition, October 1975, Wilmington, Delaware, 1975.

Ferry, J. D., Viscoelastic Properties of Polymers, John Wiley & Sons, Inc., New York, 1961.

Gillen, K. T., and K. E. Mead, "Predicting Life Expectancy and Simulating Age of Complex Equipment Using Accelerated Aging Techniques," Sandia Laboratories Reprt. SAND 79-1561, January 1980.

Hahn, H. T., Fatigue Behavior and Life Prediction of Composite Laminates, AFML-TR-78-43, Wright-Patterson AFB, Ohio, 1978.

Halpin, J. C., "Introduction to Viscoelasticity," Composite Materials Workshop, S. W. Tsai, J. C. Halpin, and N. J. Pagano, eds., Technomic Publishing Co., Westport, Conn., 1968.

Halpin, J. C., K. L. Jerina, and T. A. Johnson, "Characterization of Composites for the Purpose of Reliability Evaluation," Analysis of the Test Methods for High Modulus Fibers and Composites, ASTM STP 521, American Society for Tesing and Materials, Philadelphia, 1973, pp. 5-64.

Ho, T., The Effect of Environment on the Mechanical Behavior of AS/3501-6 Graphite-Epoxy Material, ATC Report No. B-92100/9CRL-61, Vought Corp., Dallas, 1980.

Hufferd, W., "Application of Rate Theory to Accelerated Durability Testing of Structural Adhesives," AFML-TR-79-4199, Wright-Paterson AFB, OH, March 1980.

Jackson, A. C., Advanced Manufacturing Development of Composite Empennage Component for L-1011, NAS 1-14000, Lockheed California Co., Burbank, Calif., 1975.

Jones, B. H., "Determination of Design Allowables for Composite Materials" Composite Materials: Testing and Design, ASTM STP 460, ASTM, 1969, pp. 307-320.

Jones, B. H. "Probabilistic Design and Reliability," in Composite Materials Vol. 8, Structural Design and Analysis Part II, ed. C. C. Chamis, Academic Press, 1975, pp. 34-72.

Kaminski, B. E., "Effect of Specimen Geometry on the Strength of Composite Materials," *Analysis of the Test Methods for High Modulus Fibers and Composites*, ASTM STP 521, American Society for Testing and Materials, Philadelphia, 1973, pp. 5-45.

Kapur, K. C. and L. K. Lamberson, *Reliability in Engineering Design*, Wiley, New York, 1977.

Lifshitz, J, M., "Time-Dependent Fracture of Fibrous Composites," *Composite Materials: Fracture and Fatigue*, Vol. 5, L. J. Broutman, ed., Academic Press, Inc., New York, 1974.

Lipson, C., and N. J. Sheth, *Statistical Design and Analysis of Engineering Experiments*, McGraw Hill, New York, 1972.

Magistad, J. G., "Statistical Life Testing," UCRL Report, 1981 (Number is forthcoming). LLNL Report.

McKaugue, E. L., Jr., J. E. Halkias, and J. S. Reynolds, "Moisture in Composites: The Effect of Supersonic Service on Diffusion," *J. Compos. Mater.*, *9*, 2-9, 1975.

Pagano, N. J., and R. B. Pipes, "The Influence of Stacking Sequence on Laminate Strength," *J. Composite Materials*, *5*, 50-57, 1971.

Ramkumar, R., S. Chatterjee, S. Kulkarni, and R. B. Pipes, *Definition and Modeling of Critical Flaws in Graphite Fiber Reinforced Epoxy Matrix Composite Materials*, NADC-76228-30, Materials Sciences Corp., Blue Bell, Pa., 1978.

Rotem, A., and H. G. Nelson, "Fatigue Behavior of Graphite-Epoxy Laminates at Elevated Temperature," paper presented at the Second ASTM Conference on Fatigue of Composites, San Francisco, May, 1979.

Schapery, R. A., "Stress Analysis of Viscoelastic Composite Materials," *Composite Materials Workshop*, S. W. Tsai, J. C. Halpin, and N. J. Pagano, eds., Technomic Publishing Co., Westport, Conn., 1968.

Struik, L. C. E., *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier Scientific Publishing Co., New York, 1978.

Weibull, W., "A Statistical Theory of the Strength of Materials," *Ing. Vetenskaps Akad.*, Handl. No. 151, 1939, pp. 5-45.

Yurkovsky, W., *Accelerated Testing Technology*, RADC-TR-67-420 Rome Air Development Center, Air Force Systems Command, Griffiss AFB, New York, 1967.

Zweeben, C., "The Influence of Stress Non-uniformity and Size on the Strength of Composite Structures," AIAA/ASME/ASCE/AHS 21st Structures, Structural Dynamics and Materials Conf., May 12-14, 1980.

CHAPTER VIII

NONDESTRUCTIVE EVALUATION

In order to design composite structures with confidence, it is important to be able to assess their integrity nondestructively and to evaluate their tolerance to flaws and stress concentrations. It is necessary to develop effective and practical methods of flaw detection and characterization after fabrication and in service, to monitor flaw growth under loading and environmental fluctuations, to assess flaw criticality (effects of defects), to establish accept/reject criteria, and to prescribe repair procedures.

A variety of nondestructive evaluation (NDE) techniques are being used for evaluating the integrity of composite materials. They include radiographic (X-ray and neutron), optical (moiré, photoelastic coatings, holography, and speckle interferometry), thermographic, acoustic (acoustic wave, acoustic emission), embedded sensor, and ultrasonic techniques. The various methods are best suited for detecting different types of flaws. Reviews of the state of the art of NDE of composites were given recently by Daniel and Liber (1979) and Matzkanin et al. (1979).

This chapter discusses the effects of flaws on composite strength, describes briefly the principles and applications of many currently used nondestructive techniques, and outlines recommendations for further development.

ORIGIN AND TYPES OF FLAWS

Flaws may be introduced in composite laminates during processing and fabrication. These include contaminants, voids, unpolymerized resin, nonuniform matrix distribution, incorrect fiber orientation, inclusions, ply gaps, delaminations, and crazing. Sources of stress concentration and damage growth, such as holes or cutouts of various sizes and shapes, are also introduced for design functions. Defects are also induced or enhanced in service with age, loading, and environmental conditions. These cases include matrix aging and degradation, moisture absorption, ultraviolet radiation, damage zones around initial stress concentrations, and surface gouges and scratches.

The most frequently encountered critical flaws can be classified according to the states of stress they produce in their vicinity in the following five broad categories (Parmley et al., 1978):

1. Flaws producing localized in-plane sharp stress gradients such as holes and through-the-thickness cracks;

2. Flaws producing localized through-the-thickness stress gradients such as a film patch embedded between plies;
3. Flaws producing dispersed stress gradients such as interior ply gaps; resin-rich, moisture-filled areas; or processing voids;
4. Flaws producing localized in-plane and through-the-thickness stress gradients such as deep surface scratches; and
5. Dispersed flaws such as chemically or physically degraded matrix.

FLAW CRITICALITY

The ultimate goal of all nondestructive inspection is to assess the safety and remaining useful life of the composite structure. Following the detection and characterization of defects by NDE, it is essential to assess their criticality or effect on structural behavior and strength. If flaw criticality is known and understood, then nondestructive techniques can be adapted and directed toward detecting only those flaws that have a significant influence on structural behavior. Before using NDE, therefore, it is necessary to identify the type and size of defects to be sought and characterized.

The influence of discrete flaws on composite behavior depends on many parameters, such as flaw type and geometry, orientation, lamination geometry, state of stress around the flaw, and environment. Assessment of structural integrity is based on understanding the failure mechanisms generated around flaws and the failure criteria for the basic composite material. In addition to assessing the criticality of existing flaws, it is important to study the mechanics of growth of subcritical flaws under various service conditions and thus predict if such flaws may become critical before the next scheduled inspection.

In addition to discrete flaws, general material degradation resulting from aging and environmental exposure may affect structural integrity and service life. The types and extent of degradation that can have a detrimental influence on composite behavior must be determined. Subsequently NDE techniques must be developed to detect such critical degradation.

In the case of discrete flaws, the first task needed is a reliable stress and strain analysis around realistic flaws detectable by NDE. Depending on the geometry of the flaw and the type of material response around it, this stress analysis can be analytical, experimental, or a combination of these. These analyses should account for the nonlinear response of the material and should yield stress and strain concentrations and distributions as a function of defect type and geometry. Such analyses have been conducted for defects in the form of holes of various shapes and cracks (Daniel, 1976, 1977, 1978a, 1978b; Lo and Wu, 1978, 1979; Whiteside et al., 1973).

Stress analysis must be extended into failure analysis to include the understanding and prediction of failure phenomena, modes, and damage growth around initial defects as a function of age, loading, and environment. Analytical, experimental, and semiempirical criteria have been used to explain and predict total failure in composite laminates with stress concentrations in the form of holes or cracks (Daniel, 1976, 1977, 1978a, 1978b; Lo and Wu, 1978, 1979; Whitney and Nuismer, 1974; Wu, 1975). Strength is correlated with notch (hole or crack) size, geometry, material, and type of loading.

In some cases of cracks and holes in a uniaxial stress field and in one case of holes in a biaxial stress field an average stress criterion has been found to predict the effect of notch size on strength. According to this criterion, failure occurs when the average stress over an assumed characteristic dimension from the boundary of the notch equals the tensile strength of the unnotched material (Daniel, 1976, 1977, 1978; Whitney and Nuismer, 1974). An application of this criterion to the case of uniaxially loaded graphite-reinforced epoxy laminates with holes and cracks is shown in Figure VIII-1. In a similar approach proposed by Wu (1975) and applied by Lo and Wu (1978), lamina failure criteria are used and a characteristic dimension (volume) is postulated. Failure is said to occur when the average state of stress/strain on the boundary of this characteristic volume falls on the failure envelope of the lamina. Analysis of an angle-ply laminate requires the study of progressive degradation of the various plies in the vicinity of the notch up to complete failure of the laminate. This process involves the solution of a series of stress analysis problems for the various stages of material degradation around the notch. In practice this is an unwieldy process. These analyses do not take into consideration any damage growth or delaminations around the notch, which in some cases have the beneficial effect of reducing the high-stress concentrations.

The effects of surface scratches and ply gaps have been analyzed roughly using strength-of-materials models (Lo and Wu, 1978, 1979). Attempts to analyze the influence of delaminations have not been completely successful. It is known that delaminations growing around notches do not degrade seriously the residual tensile strength of the laminate. This, of course, is not true in the case of compressive loading or tension-compression fatigue.

Most of the analytical or semiempirical predictions of strength are for mathematically defined flaws. More realistic flaws including damaged zones induced in service are very difficult to model. A significant current program deals with a study of flaw growth around damaged holes and initial damage produced by impact. Analytical methods for predicting damage growth, residual strength, and threshold damage sizes are also to be developed (Pettit and Lauraitis, 1979). Only experimental data on damage growth have been reported to date.

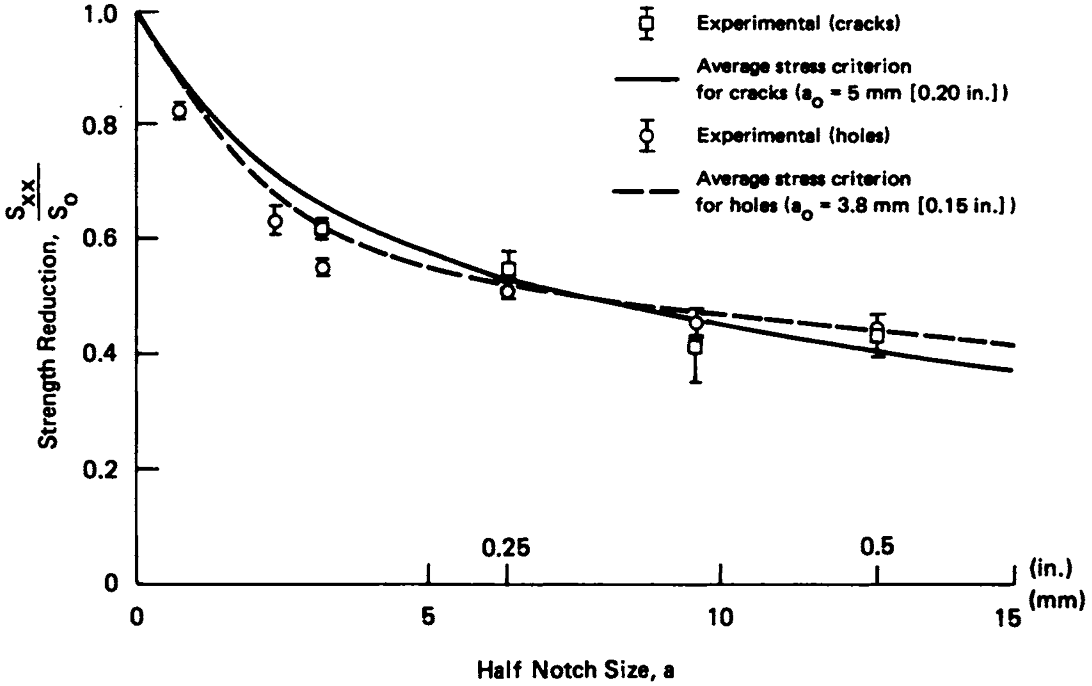


Figure VIII-1. Strength reduction as a function of notch size for $(0/\underline{+}45/90)_s$ graphite/epoxy plates with circular holes and horizontal cracks under uniaxial tensile loading

Except for cases of well-defined stress concentrators such as holes or cracks, the effects of other defects are not well known or understood. More systematic efforts employing combined experimental and theoretical approaches are necessary to assess the criticality of other types of flaws, such as irregular delaminations, matrix degradation, and matrix cracking.

Nondestructive monitoring of flaw growth for various types of initial flaws and under various loading and environmental conditions should help in developing models of flaw growth and damage accumulation in composite materials. Methods should be developed then to estimate residual strength or residual life based on flaw growth behavior.

METHODS OF FLAW DETECTION

Ultrasonic Methods

This method is the most widely used for quality control, flaw detection, and flaw growth monitoring of composite laminates (Hagemaier, 1974; Harrigan, 1978; Kulkarni et al., 1978; Liber et al., 1979; Mool and Stephenson, 1971; Pettit and Lauraitis, 1980; Rose et al., 1973; Sendeckyj et al., 1978; Sheldon, 1978; Whiteside et al., 1973). It is based on the attenuation of high-frequency sound passing through the specimen. The attenuation results from three sources, i.e., viscoelastic effects in the resin matrix, geometric dispersion caused by material heterogeneity, and geometric attenuation caused by internal defects such as delaminations and cracks. The effects of the latter are maximized by proper selection of the sound wave frequency.

The transducers and the specimen are immersed in a tank of water to provide a uniform coupling medium for transmission of the ultrasonic waves. In some applications to large components in the aerospace industry the parts are not immersed. Coupling medium is provided by a steady jet of water bridging the gap between the transducer and part.

In the pulse echo mode the ultrasound transmitted by the single transducer is received by the same transducer after reflection from the back surface of the specimen. The attenuation of the reflected pulse is related to internal defects in the laminate. In the through-transmission mode two transducers are used: a transmitting one in front of the specimen and a receiving one in the back of the specimen.

Ultrasonic inspection records can be obtained in many forms such as an amplitude-time display for a specific point on the specimen (A-scan), amplitude curve along a scan line (B-scan), and a series of scans covering the surface of the specimen and giving a plan view image (C-scan). Two modes of recording the ultrasonic signal strength have been used primarily. The first mode called the analog mode, is a combination of B- and C-scanning. The gated peak voltage of the reflected pulse is recorded by a deflection of the pen normal to the scanning direction. The variations of this voltage are related to the presence of flaws. A typical analog record of a specimen with an embedded patch is shown in Figure VIII-2a. In the second mode (C-scan) an alarm circuit with two limits is used. The limits are adjusted to lift the pen of the X-Y recorder whenever the gated peak voltage becomes smaller or larger than certain values corresponding to known flaws of a standard specimen. A typical record of this type for the same specimen is shown in Figure VIII-2b. The oscilloscope displays of the pulse (A-scans) serve as an essential guide in recording the scans and in subsequent interpretation and analysis.

In assessing the integrity of a composite laminate one must be able to determine nondestructively thickness, fiber orientation, volume fraction, and flaws. The pulse-echo technique is ideal for measuring thickness. The applicability of ultrasonics in detecting fiber content and orientation has not been fully explored yet. The flaws most easily detected by ultrasonics are delaminations, inclusions, and surface scratches. In some cases voids and porosity clusters may be detected (Judd and Wright, 1978; Martin, 1976). Ultrasonics has also been used to evaluate strength degradation in glass-reinforced epoxy as a result of environmental exposure (Meron et al., 1977).

Computer-aided procedures have been developed for recording and for more sophisticated processing of ultrasonic data (Elsley, 1978). Plotting of the data in any desired form can be done at any time after inspection using different discriminator levels to detect smaller or larger flaws.

In addition to the laboratory applications previously discussed, it is of great importance to develop procedures for in-service inspection of composite structures. One of the most difficult problems to overcome in this case is that of adequate and consistent coupling between transducer and structure. The location coordinates of the transducer in one application are sensed by means of a sonic stylus attached to the transducer and two linear microphones located along two (X- and Y-) reference axes of the structure (Chang, 1977). The ultrasonic data from the pulser/receiver and position data are recorded and processed through a minicomputer and then are plotted in the form of C-scans.

Radiographic Methods

A variety of X-ray radiographic techniques has been applied to composite materials (Chang et al., 1975; Domanus and Lilholt, 1978; Maigret and Jube, 1971; Sendeckyj et al., 1978). Radiographic methods were applied to the study of fatigue damage around holes in angle-ply boron-reinforced epoxy laminates (Roderick and Whitcomb, 1976). X-ray radiographs clearly show the sites of fiber breaks in thin laminates.

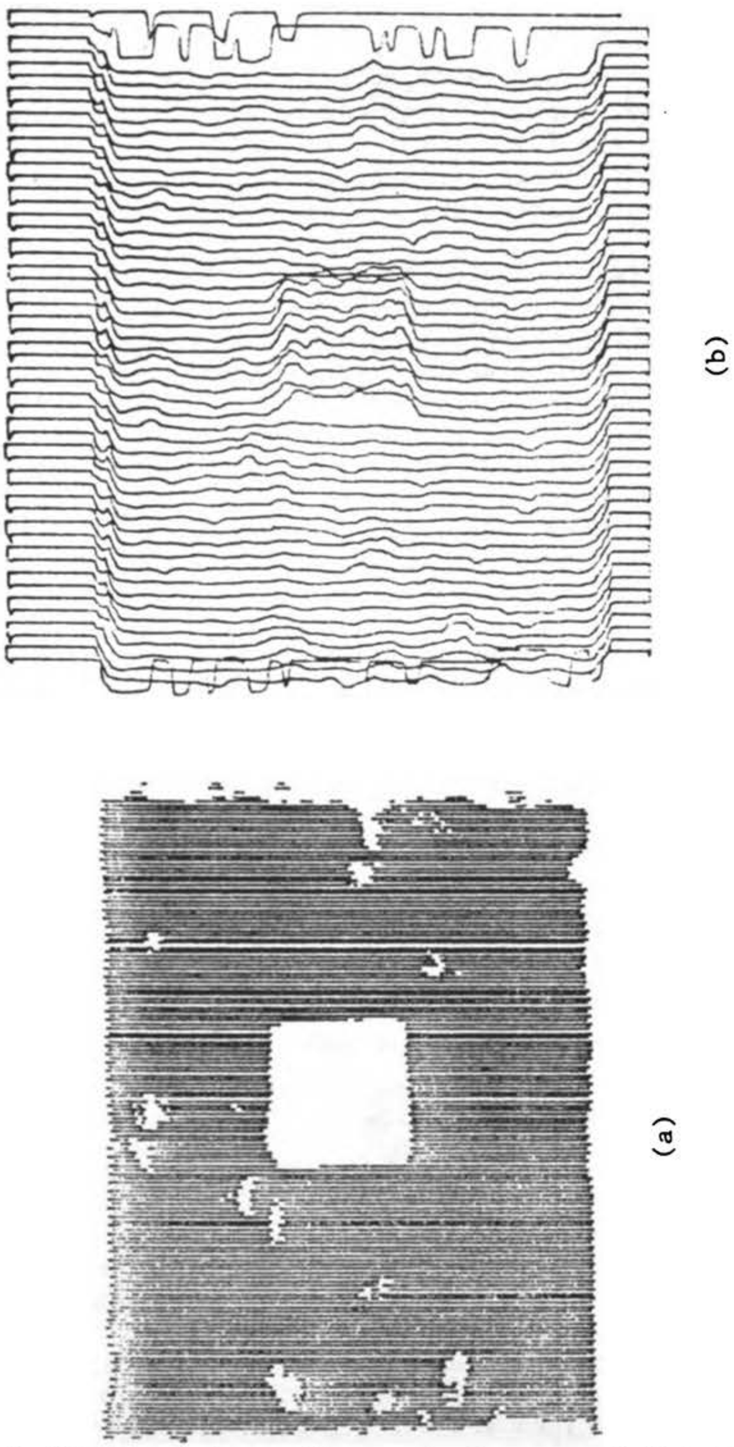


Figure VIII-2 Representative ultrasonic C-scans of the same $[0/\pm45/90]_{2s}$ graphite/epoxy specimen with an initial flaw in form of an embedded interply square film patch. (a) Pen-Lift Scan. (B) Analog Scan.

Low-voltage radiography with soft X-rays was found particularly suitable for NDE of graphite fiber composites (Domanus and Lilholt, 1978). Defects in the form of voids as small as 0.1 mm (4×10^{-3} in.) can be detected. Metallic inclusions as small as a 5-μm (2×10^{-4}-in.) diameter tungsten wire can be easily detected.

The most effective means of detecting damage consisting of cracks and delaminations in graphite-reinforced epoxy and hybrid composites is by enhancing the X-ray method with tetrabromoethane (Chang et al., 1975). This is an X-ray opaque fluid that penetrates into the delaminations and matrix cracks and enhances the radiographic image of the damage. Fine details of the damage detected by this technique are illustrated in Figure VIII-3, which shows the damage zones growing from the edges of circular holes in fatigue tested $[(0/\pm45/90)_s]_2$ graphite-reinforced epoxy specimens (Sendeckyj et al., 1978). The damage zones consist of delaminations (diffuse splotchy areas) and a pattern of regularly spaced cracks.

In general, X-ray radiography enhanced with opaque penetrants gives detailed information on fiber orientation, fiber fractures, matrix cracks, and delaminations. It gives only planar information (no depth). There is a need to develop procedures of enhanced X-ray stereoscopic NDE giving through-the-thickness flaw information. At present, flaws are detected only when they extend to a free surface where they are exposed to the penetrant. A new effective and nontoxic penetrant is needed to replace the toxic tetrabromoethane. It has been suggested that diiodobutane (DIB) is a more desirable penetrant.

Neutron radiography is also being proposed as a NDE technique for composites (Dance and Middlebrook, 1979). However, this technique has only been used to provide demonstrations of feasibility.

Acoustic Emission

The acoustic emission method is based on the phenomenon that the sudden release of energy inside a material results in emission of acoustic pulses. Energy release occurs as a result of deformations or failure processes caused by loading. The primary failure mechanisms in fiber composites are matrix cracking, fiber debonding, and fiber breakage. The acoustic signals are detected by piezoelectric transducers in contact with the specimen through a coupling medium, electronically processed, and recorded. The usual procedure is to count the number of pulses above a preset amplitude threshold. The result can be recorded and presented in terms of cumulative number of counts, which indicates the extent of damage, or rate of counts, which is related to the rate of damage growth. The various failure mechanisms in composites produce signals of different amplitudes. Thus, fiber breakage produces a higher acoustic emission activity than fiber debonding, which in turn produces more measurable counts than matrix cracking.

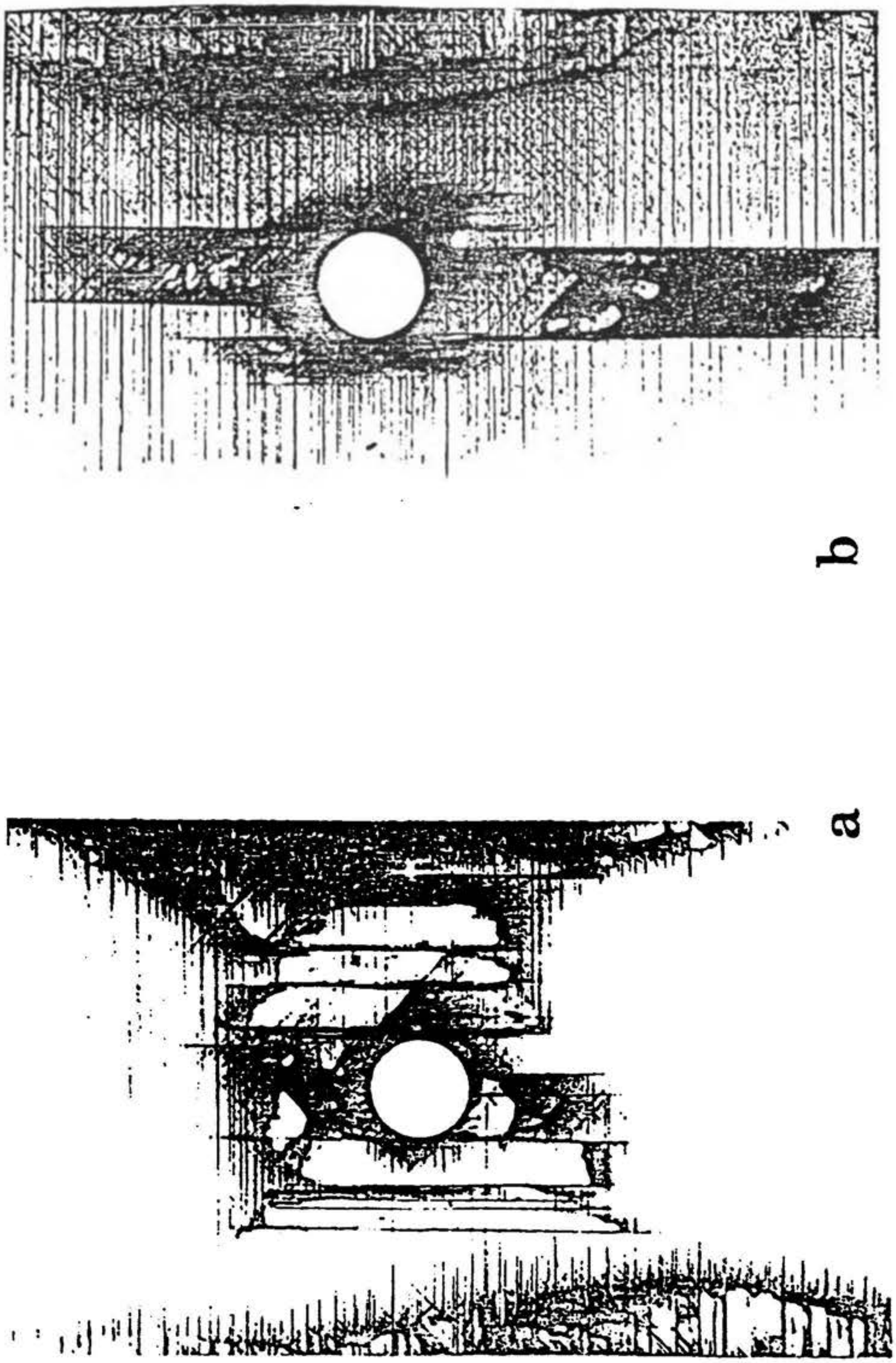


Figure VIII-3 TBE enhanced x-ray photographs showing fatigue induced damage in $[(0/\underline{+}45/90)_s]_2$ graphite-epoxy specimens

To be able to detect and discriminate defects and fracture modes, it is not sufficient to measure number and rate of acoustic emission counts. Attempts have been made to discriminate and identify the various microfracture modes by amplitude distribution and frequency analysis of the acoustic pulses (Rotem, 1977). Computer pattern recognition techniques have been used to analyze acoustic emission signals and to correlate frequency and amplitude distributions with physical and mechanical properties of the composite material, such as moisture content and strength (Graham and Elsley, 1978). To date, however, no quantitative failure criteria exist in terms of easily measurable acoustic emission parameters.

Optical Methods

Visual Inspection

The most obvious method in this group is visual inspection of composite panels. The visibility of surface flaws, such as scratches and fiber breaks, can be enhanced with appropriate lighting and dye penetrants. The process can be further improved by the use of television cameras for remote and systematic inspection. Fluorescent penetrants combined with microscopic examination make a useful tool for determining fiber patterns, broken fibers, and resin-rich areas.

Moiré Method

An optical method that has been used successfully in measuring localized deformations and flaw growth in composites is the moiré method (Armenakas et al., 1972; Chiang and Slepetz, 1973; Daniel, 1975, 1976, 1977, 1978a, 1978b; Daniel and Rowlands, 1971, 1972; Daniel et al., 1973; Pipes and Daniel, 1971; Rowlands et al., 1973). It is a full-field technique based on the interference of two closely spaced arrays of lines, one array attached to the specimen and the other used as reference.

Moiré techniques are well suited for the study of crack growth. Figure VIII-4 illustrates the application of this method to the detection of crack growth in a composite specimen. In general, the method is limited to detecting surface or near-surface defects, and it lacks adequate sensitivity.

Photoelastic Coating Method

The photoelastic or birefringent coating method consists of bonding on the specimen surface a thin coating of birefringent material with reflective cement at the interface. When the specimen is loaded, the surface strains are transmitted to the coating and produce a fringe pattern that is viewed or recorded and analyzed by means of a reflection polariscope. Applications of birefringent coatings to glass-reinforced epoxy composites have been described by Dally and Alfirevich

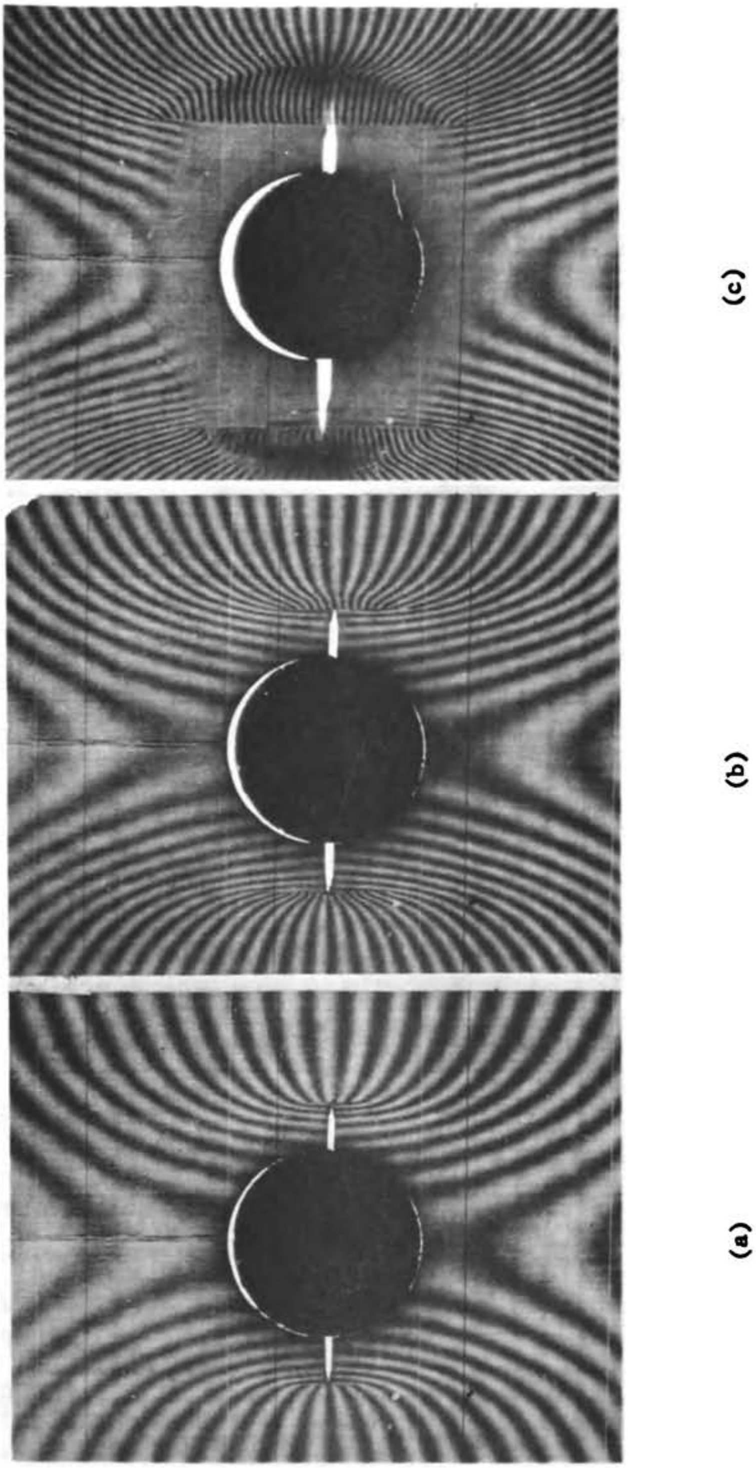


Figure VIII-4 Moiré fringe patterns around crack in glass-epoxy composite [0/90/0/$\overline{90}$] at three levels of applied stress, (a) σ = 11,000 psi, (b) σ = 14,800 psi, (c) σ = 18,500 psi

(1969). Similar applications to glass-, boron-, and graphite-reinforced epoxy composites were described by Daniel (1975, 1976, 1977, 1978a, 1978b), Daniel and Rowlands (1972); and Daniel et al. (1973b, 1974).

Photoelastic coatings are very sensitive in detecting localized strain concentrations and damage growth in composites. Although photoelastic coatings are much more sensitive than moire grids, they cannot be used as a practical means for long-term monitoring of defect growth because of their sensitivity to environmental fluctuations. Like the moiré method, the birefringent coating method is mainly suitable for detecting surface or near-surface defects.

Holographic Methods

The holographic method is based on the optical interference produced by superposition of coherent light waves reflected from the object under consideration (object beam) and those of a coherent reference beam. The laser is an ideal source of coherent monochromatic light. The normal procedure is to record the interference pattern on film (hologram) and subsequently view it with a similar laser beam. The emerging light from the hologram contains the wave patterns characteristic of the original object.

One of the important applications of holography to structural and stress analysis is interferometry, i.e., the measurement of small surface displacements in a body produced by mechanical or thermal loadings. In applying holographic interferometry, two holograms of the test object are recorded on the same photographic plate with an alteration of the object surface occuring between the two recordings.

For a helium-neon laser, the sensitivity of holographic interferometry in measuring surface displacements is approximately 0.3 μm (1.2×10^{-5} in.). In addition to its full-field nature and high sensitivity, the method has the added advantage that it does not require any special surface preparation and can be applied readily to surfaces such as those of composites (Erf, 1974; Maddux and Sendeckyj, 1979; Rowlands and Daniel, 1972; Sendeckyj et al., 1978).

Holographic techniques commonly used in experimental mechanics fall into four basic categories: (1) double exposure holographic interferometry, (2) real-time holographic interferometry, (3) time-average or vibration holographic interferometry, and (4) dynamic double-exposure pulsed holographic interferometry.

An important application of holography is NDE of material integrity. The technique relies on the fact that if the state of stress in the component is changed, the surface displacements will be altered locally around surface or near surface defects. This alteration is manifested as a local anomaly in the overall fringe pattern.

This nondestructive detection is performed either by double- exposure or real-time holography. Cracking and delamination in composite laminates and bond defects in composite sandwich panels or adhesive joints can be detected. The type of loading applied to reveal the presence of a defect depends on the type of defect sought, the material properties, and the component geometry.

Double-exposure holographic techniques have been used to detect fatigue-induced damage around circular holes and cracks in composite laminates (Sendeckyj et al., 1978). Fatigue-induced damage and stiffness loss were also detected by holographic interferometry (Nevadunsky et al., 1975). Double-pulse holography was also used to detect disbonds and delaminations in composite compressor blades by subjecting them to acoustic excitation (Erf et al., 1972).

Holography is an effective NDE technique for composite materials; it is capable of detecting delaminations and cracks in the surface plies Maddux and Sendeckyj, 1979). It is capable of detecting both matrix cracks and fiber breaks in the surface plies and can give some information relative to the through-the-thickness distribution of delaminations. It does not, however, detect subsurface matrix cracking. It is capable of detecting flaws near free edges but not other subsurface flaws. The potential of the method has not been fully developed. More work is necessary to interpret fringe patterns produced by a variety of excitation techniques.

Speckle Interferometric Method

Speckle interferometry makes use of the speckle pattern produced on the surface of an object illuminated by coherent light. It has many characteristics complementary to those of holographic interferometry. It is less sensitive than the latter and is primarily indicative of in-plane displacements.

Leendertz (1970) described a technique in which the object surface is illuminated by two coherent beams equally inclined from the normal to the surface. An alternative method has been proposed by Archbold et al. (1970) in which the object is illuminated by one beam and two exposures are recorded, before and after loading. These techniques were further generalized by Hung and Hovanesian (1972) to three-dimensional cases.

The most important development in this area is that of speckle-shearing interferometry introduced by Hung and Taylor 1973). This technique allows direct determination of derivatives of surface displacements. It overcomes or alleviates many of the limitations of conventional interferometry, namely: (1) the setup is relatively simple and does not require laborious alignment of optics, (2) mechanical and environmental stability are not critical, (3) coherent length of light is minimized, (4) sensitivity can be controlled over a wider range, (5) films of much lower resolution can be used, (6) the fringes always localize on the specimen surface, and (7) strains can be recorded directly without the need of differentiating displacements. More recent developments introduced by Hung et al., (1975, 1978) allow the simultaneous determination of derivatives of surface displacements along any direction and with variable sensitivity using a single photographic record (shearing-specklegram).

Speckle-shearing interferometry can be applied effectively to testing of composite materials. The feasibility of the method as a NDE tool has been demonstrated (Hung and Hovanesian, 1979), but the full potential of the method for nondestructive evaluation of composites has not been fully explored.

Thermographic Methods

The high sensitivity of liquid crystals to heat and their property of scattering visible radiation make them suitable for detecting flaws or fractures in composites. Local delaminations resulting in nonuniform heat conduction and fatigue fractures producing localized heat are easily manifested with liquid crystal coatings (Broutman et al., 1969; Charles, 1978; Maigret and Jube, 1971; Nevadunsky et al., 1975).

Similar to the liquid crystal coating technique in its application, although different in principle, is IR scanning. Advanced instrumentation is now commercially available that makes IR scanning techniques practical and valuable in production-type inspection of composite honeycomb panels and composite laminates. Disbonds, delaminations, and other defects can be viewed as discontinuities in heat conduction and IR radiation and can be recorded with an infrared camera (Reifsnider and Williams, 1974).

In general, thermographic methods can detect the presence of various flaws but do not give a clear definition of them.

Embedded Sensor Techniques

Internal deformations in composite laminates and structures during curing and throughout service life can be monitored continuously with embedded strain gages supplemented with embedded thermocouples. Techniques for embedding such sensors in composite laminates and recording and interpreting the results have been developed and applied (Daniel and Liber, 1975; Daniel et al., 1972). These techniques have been used to monitor the buildup of lamination residual stresses in angle-ply laminates during curing and the internal deformations during subsequent environmental and loading cycles. They can also be used for continual monitoring of composite structures in service for signs of structural degradation.

Other Techniques

Electromagnetic techniques using microwaves have been used in glass-reinforced epoxy composites. Results to date have not been very conclusive. One of the major problems is that of composite material degradation caused by exposure to high humidity and temperature. To date no suitable NDE techniques exist for measuring moisture absorption and matrix degradation. One method based on measuring effusing moisture and solving the diffusion equation has been proposed (Kaelble and Dynes, 1977). Another method proposed for the purpose is nuclear magnetic resonance (O'Meara and Rollwitz, 1954), but it would be very difficult to apply under field conditions.

Bulk properties of strength and stiffness and their degradation can best be measured using vibration or wave propagation techniques. These techniques involve the measurement of dynamic moduli and attenuation coefficients. Material damage or degradation affects these properties. A stress wave technique was proposed by Vary and Lark (1978) for predicting tensile strength and evaluating effects of microporosity and variations in fiber volume content.

CONCLUSIONS

1. Flaws in composites may be introduced during processing and fabrication (contaminants, voids, unpolymerized resin, nonuniform matrix distribution, incorrect fiber orientation, inclusions, ply gaps, delaminations, and crazing), and they may be induced or enhanced in service (matrix aging and degradation, moisture absorption, ultraviolet radiation, damage zones around initial stress concentrations, and surface checks and scratches).

2. The most frequently occurring critical flaws are typified by delamination cutouts, embedded patches, interior ply gaps, and surface scratches.

3. The criticality of flaws or effects of defects on stiffness and strength, especially irregular or dispersed flaws, are not well known and understood.

4. A variety of NDE techniques are applicable to composites. They include radiographic (X-ray and neutron), holographic, thermographic, acoustic (acoustic wave, acoustic emission), photomechanical (moiré and photoelastic coating), embedded sensor, and ultrasonic techniques.

5. The most commonly used method is ultrasonics (through-transmission, pulse echo). This method is most suitable for detecting delaminations, inclusions, and surface scratches.

Other types of flaws, however, are not easily detectable by conventional ultrasonic techniques. Considerable progress has been noted in computer-aided inspection and data processing.

6. X-ray radiography enhanced with opaque penetrants gives detailed information on fiber orientation, fiber fractures, matrix cracks, and delaminations. It gives only planar information (no depth).
7. Holography can detect delaminations and surface-ply cracks.
8. Photomechanical techniques (moiré and photoelastic coatings) are mainly suitable for detecting surface or near-surface defects.
9. Thermographic techniques can detect the presence of various flaws but do not give a clear definition of them.
10. Stiffness degradation caused by a variety of flaws can be detected by acoustic wave, vibration, and embedded sensor techniques.

RECOMMENDATIONS

1. Stress and strain analyses (analytical and experimental) should be conducted around realistic flaws detectable by NDE. Stress concentrations and stiffnesses should be determined as a function of flaw size and geometry.
2. Failure analyses (analytical, experimental, and semiempirical) should be conducted to correlate strength with defect size and geometry.
3. Efforts should be devoted to monitoring, understanding, and modeling flaw growth in composite structures subjected to service loading and environmental conditions.
4. Methods should be developed to estimate residual strength or residual life based on flaw-growth behavior.
5. Effects of chemical and physical matrix degradation on stiffness, strength, and residual life should be studied.
6. Better communication is desired between NDE technologists and composite mechanicians.

7. Further development is needed of various NDE techniques applicable to composites with a better understanding of the advantages and limitations of each technique. Results of the various techniques should be correlated.

8. Full-field inspection methods (acoustic, holography, phased array, and radiographic methods) should be developed.

9. Further developments are necessary in NDE data acquisition, processing, and interpretation. Techniques should be developed for reliable flaw definition and characterization. Destructive testing can be used in developing such techniques.

10. Specimens with realistic "standard" or "reference" flaws are needed for system calibration.

11. There is need for further development of portable equipment and techniques for field inspection of composite structures and for the elimination of subjectivity from such measurements.

12. Reliable techniques are needed for detecting dispersed types of flaws such as moisture absorption and matrix degradation.

13. Procedures of enhanced stereoscopic X-ray photography giving through-the-thickness flaw information should be developed.

14. The potential of holography and speckle interferometry as practical NDE tools should be investigated further.

REFERENCES

Archbold, E., J. M. Burch, and A. E. Ennos, "Recording of In-Plane Surface Displacement by Double-Exposure Speckle Photography," *Opt. Acta*, *17*(12), 883-898, (1970).

Armenakas, A. E., S. K. Garg, C. A. Sciammarella, and V. Svalbonas, "Experimental Study of the Failure Mechanism and Strength Characteristics of Fiber Bundles and Composites," *Exper. Mech.*, *12*, 1-10, (1972).

Broutman, L. J., T. Kobayashi, and D. Carrillo, "Determination of Fracture Sites in Composite Materials with Liquid Crystals," *J. Compos. Mater.*, *3*, 702-704, (1969).

Chang, F. H., "In-Service Inspection of Advanced Composite Aircraft Structure," AFML Contract No. F33615-77-C-5206, 1977.

Chang, F. H., J. C. Couchman, J. R. Eisenmann, B. G. W. Yee, "Application of a Special X-Ray Nondestructive Testing Technique for Monitoring Damage Zone Growth in Composite Laminates," *Composite Reliability*, ASTM STP 580, American Society for Testing and Materials, Philadelphia, 1975, pp. 176-190.

Charles, J. A., "Use of Liquid Crystals in Detecting Fatigue Damage," paper presented at 1978 Society for Experimental Stress Analysis (SESA) Spring Meeting, Wichita, Kans., May, 1978.

Chiang, F. P., and J. Slepetz, "Crack Length Measurements in Composites," *J. Compos. Mater.*, *7*, 134-137 (1973).

Dally, J. W., and I. Alfirevich, "Application of Birefringent Coatings to Glass-Fiber-Reinforced Plastics," *Exper. Mech.*, *9*, 97-102, (1969).

Dance, W. E. and J. B. Middlebrook, "Neutron Radiographic NDI for Bonded Composite Structures," *Nondestructive Evaluation and Flaw Criticality for Composite Materials*, ASTM STP 696, R. B. Pipes, ed., American Society for Testing and Materials, Philadelphia, pp. 57-71.

Daniel, I. M., "Optical Methods for Testing Composite Materials," paper presented at 39th Meeting of the Structures and Materials Panel on "Failure Modes of Composite Materials with Organic Matrices and Their Consequences on Design," AGARD-NATO, Munich, Germany, October 6-12, 1974, AGARD-CP-163, 1975.

Daniel, I.M., *Biaxial Testing of Graphite/Epoxy Composites Containing Stress Concentrations*, Part I, AFML-TR-76-244, December 1976.

Daniel, I. M., *Biaxial Testing of Graphite/Epoxy Composites Containing Stress Concentrations*, Part II, AFML-TR-76-244, June 1977.

Daniel, I. M., "Strain and Failure Analysis of Graphite/Epoxy Plates with Cracks," *Exper. Mech.*, *18*(7), 246-252 (1978a).

Daniel, I. M., "Deformation and Failure of Composite Laminates with Cracks in Biaxial Stress Fields," *Proceedings of the SixthInternational Conference on Experimental Stress Analysis*, Munich, Germany, September 18-22, VDI Berichte, Nr. 313, 1978b, pp. 705-710.

Daniel, I. M., and T. Liber, *Lamination Residual Stresses in Fiber Composites*, NASA CR-134826, NASA-Lewis Research Center, Cleveland, 1975.

Daniel, I. M., and T. Liber, "Nondestructive Evaluation Techniques for Composite Materials," Proceedings of the *12th Symposium on Nondestructive Evaluation*, San Antonio, April 24-26, 1979.

Daniel, I. M, J. L. Mullineaux, F. J. Ashimaz, and T. Liber, "The Embedded Strain Gage Technique for Testing Boron/Epoxy Composites," *Composite Materials: Testing and Design*, ASTM STP 497, American Society for Testing and Materials, Philadelphia, 1972, pp. 257-272.

Daniel, I. M., and R. E. Rowlands, "Determination of Strain Concentration in Composites by Moiré Techniques," *J. Compos. Mater.*, *5*, 250-254 (1971).

Daniel, I. M., and R. E. Rowlands, "Experimental Stress Analysis of Composite Materials," ASME Paper No. 72-DE-6 presented at American Society of Mechanical Engineers Design Engineering Conference, Chicago, 1972.

Daniel, I. M., R. E. Rowlands, and D. Post, "Strain Analysis of Composites by Moiré Methods," *Exper. Mech.*, *13*(6), 246-252 (1973).

Daniel, I. M., R. E. Rowlands, and J. B. Whiteside, "Deformation and Failure of Boron-Epoxy Plate with Circular Hole," *Analysis of the Test Methods for High Modulus Fibers and Composites*, ASTM STP 521, American Society for Testing and Materials, Philadelphia, 1973b, pp. 143-164.

Daniel, I. M., R. E. Rowlands, and J. B. Whiteside, "Effects of Material and Stacking Sequence on Behavior of Composite Plates with Holes," *Exper. Mech.*, *14*, 1-9 (1974).

Domanus, J. C., and H. Lilholt, "Nondestructive Control of Carbon Fibre Reinforced Composites by Soft X-ray Radiography," *Proceedings of the 1978 International Conference on Composite Materials*, ICCM/2 the American Institute of Mining, Metallurgical, and Petroleum Engineers, Toronto, Canada, April 16-20, 1978, pp. 1072-1092.

Elsley, R. K., "Computer Aided Interpretation of NDE Signals," *Proceedings of the ARPA/AFML Review of Progress in Quantitative NDE*, AFML-TR-78-55, Air Force Materials Laboratory, May 1978, pp. 326-330.

Erf, R. K., ed., Holographic Nondestructive Testing, Academic Press, Inc., New York, 1974.

Erf, R. K., J. P. Waters, R. M. Gagosz, F. Michael, and G. Whitney, Nondestructive Holographic Techniques for Structures Inspection, AFML-TR-72-204, Air Force Materials Laboratory, October 1972.

Graham, L. J., and R. K. Elsley, "Characteristics of Acoustic Emission Signals from Composites," Proceedings of the ARPA/AFML Review of Progress in Quantitative NDE, AFML-TR-78-55, Air Force Materials Laboratory, May 1978, pp. 219-225.

Hagemaier, D., "Ultrasonic Applications in the Aerospace Industry," SAE Trans., 83, 2767-2796, (1974).

Harrigan, W. C., Jr., "Ultrasonic Inspection of Graphite/Aluminum Composites," Proceedings of the 1978 International Conference on Composite Materials, ICCM/2, Toronto, Canada, April 16-20, 1978, pp. 1123-1140.

Hung, Y. Y., I. M. Daniel, and R. E. Rowlands, "Full-Field Optical Strain Measurement Having Postrecording Sensitivity and Direction Selectivity," Exper. Mech., 18(2), 56-60 (1978).

Hung, Y. Y., and J. D. Hovanesian, "Full-Field Surface-Strain and Displacement Analysis of Three-Dimensional Objects by Speckle Interferometry," Exper. Mech., 12, 454-460 (1972).

Hung, Y. Y. and J. D. Hovanesian, "Nondestructive Testing by Speckle-Shearing Interferometry," Proceedings of the 12th Symposium on Nondestructive Evaluation, San Antonio, April 24-26, 1979.

Hung, Y. Y., R. E. Rowlands, and I. M. Daniel, "A Speckle-Shearing Interferometric Technique: A Full-Field Strain Gage," Appl. Opt. 14, 618-622 (1975).

Hung, Y. Y., and C. E. Taylor, "Speckle-Shearing Interferometric Camera--A Tool for Measurement of Derivatives of Surface Displacement," Proceedings of the Society of Photo-Optical Instrumentation Engineers, Vol. 41, San Diego, August 27-29, 1973, pp. 169-176.

Judd, N. C., and W. W. Wright, "Voids and Their Effects on the Mechanical Properties of Composites--An Appraisal," SAMPE J., 14(1), 10-14 (1978).

Kaelble, D. H. and P. J. Dynes, "Methods for Detecting Moisture Degradation in Graphite-Epoxy Composites," Mater. Eval., 35(4), 103-108 (1977).

Kulkarni, S. V., R. B. Pipes, R. L. Ramkumar, and W. R. Scott, "The Analytical Experimental and Nondestructive Evaluation of the Criticality of an Interlaminar Defect in a Composite Laminate," *Proceedings of the 1978 International Conference on Composite Materials*, ICCM/2, Toronto, Canada, April 16-20, 1978.

Leendertz, J. A., "Interferometric Displacement Measurement on Scattering Surfaces Utilizing Speckle Effect," *J. Sci. Instrum.* *3*, 214, (1970).

Liber, T., I. M. Daniel, and S. W. Schramm, "Ultrasonic Techniques for Inspecting Flat and Cylindrical Composite Specimens," *Nondestructive Evaluation and Flaw Criticality for Composite Materials*, ASTM STP 696, R. B. Pipes, ed., American Society for Testing and Materials, Philadelphia, 1979, pp. 5-25.

Lo, K. H., and E. M. Wu, "Failure Strength of Laminates," *Advanced Composite Serviceability Program*, Contract No. F33615-76-C-5344, Air Force Materials Laboratory, Quarterly Reports 5 through 10, 1978, 1979.

Maddux, G. E., "Photomechanics Facility," Air Force Flight Dynamics Laboratory, Dayton, 1976.

Maddux, G. E., G. P. Sendeckyj, "Holographic Techniques for Defect Detection in Composite Materials," *Nondestructive Evaluation and Flaw Criticality for Composite Materials*, ASTM STP 696, R. B. Pipes, ed., American Society for Testing and Materials, Philadelphia, 1979, pp. 26-44.

Maigret, J. P., and G. Jube, "Advanced NDT Methods for Filament Wound Pressure Vessels and Composites in General," SAMPE, Sci. Advan. Mater. Process Eng. Ser., *16*, 123-137 (1971).

Martin, B. G., "Ultrasonic Attenuation Due to Voids in Fiber-Reinforced Plastics," *Nondestr. Test. Int.* *9*(5), 242-246 (1976).

Matzkanin, G. A, G. L. Burkhardt, and C. M. Teller, *Nondestructive Evaluation of Fiber Reinforced Epoxy Composites--A State-of-the-Art Survey*, Contract No. DLA 900-77-C-3733, Southwest Research Institute for U.S. Army Aviation, April 1979.

Meron, M., Y. Bar-Cohen, and O. Ishai, "Nondestructive Evaluation of Strength Degradation in Glass-Reinforced Plastics as a Result of Environmental Effects," *J. Test. Eval.*, *5*(5), 394-396 (1977).

Mool, D., and R. Stephenson, "Ultrasonic Inspection of a Boron/Epoxy-Aluminum Composite Panel," *Mater. Eval.* *29*(7), 159-164 (1971).

Nevadunsky, J. J., J. J. Lucas, and M. J. Salkind, "Early Fatigue Damage Detection in Composite Materials," *J. Compos. Mater. 9*, 394-408 (1975).

O'Meara, J. P., and W. L. Rollwitz, "Determination of Moisture by Nuclear Magnetic Resonance," *Proc. Instrum. Soc. Amer. 9*(2), Paper No. 54-19-1, 1954.

Parmley, P. A., D. Y. Konishi, and K. E. Hofer, "On the Accelerated Testing of Graphite/Epoxy Coupons," *Proceedings of the 1978 International Conference on Composite Materials*, ICCM/2, Metallurgical Section of the American Institute of Mining, Metallurgical and Petroleum Engineers, Toronto, Canada, April 16-20, 1978, pp. 1604-1619.

Pettit, D. E., and K. N. Lauraitis, *Residual Strength Degradation for Advanced Composites*, Interim Technical Quarterly Reports, LR 28360-1 to LR 28360-17, Contract No. F33615-77-C-3084, Lockheed-California Co., Burbank, Calif., November 1977 to August 1980.

Pipes, R. B. and I. M. Daniel, "Moiré Analysis of the Interlaminar Shear Edge Effect in Laminated Composites," *J. Compos. Mater.* (5), 255-259 (1971).

Reifsnider, K. L., and R. S. Williams, "Determination of Fatigue-Related Heat Emission in Composite Maerials," *Exper. Mech. 14*(12), 479-485 (1974).

Roderick, G. L., and J. D. Whitcomb, *Fatigue Damage of Notched Boron/Epoxy Laminates Under Constant Amplitude Loading*, NASA TM X-73994, December 1976.

Rose, J. L, J. M. Carson, and D. J. Leidel, "Ultrasonic Procedures for Inspecting Composite Tubes," *Analysis of the Test Methods for High Modulus Fibers and Composites*, ASTM STP 521, American Society for Testing and Materials, 1973, pp. 311-325.

Rotem, A., "The Discrimination of Micro-Fracture Mode of Fibrous Composite Material by Acoutic Emission Technique," *Fibre Sci. 10*, 101-121 (1977).

Rowlands, R. E., and I. M. Daniel, "Application of Holography to Anisotropic Composite Plates," *Exper. Mech. 12*(2), 75-82 (1972).

Rowlands, R. E., I. M. Daniel, and J. B. Whiteside, "Stress and Failure Analysis of a Glass-Epoxy Plate with a Hole," *Exp. Mech. 13*, 31-37 (1973).

Rowlands, R. E., I. M. Daniel, and J. B. Whiteside, "Geometric and Loading Effect on Strength of Composite Plates with Cutouts," *Composite Materials: Testing and Design (Third Conference)*, ASTM STP 546, American Society for Testing and Materials, Philadelphia, 1974, pp. 361-375.

Schwalbe, H. J., "Acoustic Emission as an Aid for Inspecting GFRP Pressure Tubes," Proceedings of the 1978 International Conference on Composite Materials, ICCM/2, Metallurgical Section of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Toronto, Canada, April 16-20, 1978.

Sendeckyj, G. P., G. E. Maddux, and N. A. Tracy, "Comparison of Holographic, Radiographic and Ultrasonic Techniques for Damage Detection in Composite Materials, Proceedings of the 1978 International Conference on Composite Materials, ICCM/2, Metallurgical Section of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Toronto, Canada, April 16-20, 1978, pp. 1037-1056.

Sheldon, W. H., "Comparative Evaluation of Potential NDE Techniques for Inspection of Advanced Composite Structures," Mater. Eval., 36(2), 41-46 (1978).

Vary, A., and K. J. Bowles, "An Ultrasonic-Acoustic Technique for Nondestructive Evaluation of Fiber Composite Strength," Proceedings of the 33rd Annual Technical Conference, 1978, Sec. 24-A, Reinforced Plastics/Composites Institute, The Society of Plastics Industry, Inc., New York.

Vary, A., and R. F. Lark, "Correlation of Fiber Composite Tensile Strength with the Ultrasonic Stress Wave Factor," NASA TM-78846, paper presented at 1978 Spring Conference of the American Society for Nondestructive Testing, April 1978.

Whiteside, J. B., I. M. Daniel, and R. E. Rowlands, "The Behavior of Advanced Filamentary Composite Plates with Cutouts," AFFDL-TR-73-48, Air Force Flight Dynamics Laboratory, Dayton, June 1973.

Whitney, J. M., and R. J. Nuismer, "Stress Failure Criteria for Laminated Composites Containing Stress Concentrations," J. Compos. Mater., 8, 253-265 (1974).

Wu, E. M., "Failure Criteria to Fracture Mode Analysis of Composite Laminates," AGARD-CP-163, North Atlantic Treaty Organization, 1975.