

CRZ

AD-A149 010

312 100 000

1

DTIC
ELECTE
JAN 03 1985
S E D

This document has been approved
for public release and since its
distribution is unlimited.

84 12 21 063

**NATIONAL RESEARCH COUNCIL
COMMISSION ON ENGINEERING AND TECHNICAL SYSTEMS
NATIONAL MATERIALS ADVISORY BOARD**

The purpose of the National Materials Advisory Board
is the advancement of materials science and engineering in the national interest.

CHAIRMAN

Dr. Arden L. Bement, Jr.
Vice President, Technical
Resources
Science and Technology Department
TRW, Inc.
23555 Euclid Ave.
Cleveland, OH 44117

PAST CHAIRMAN

Dr. Donald J. McPherson
(Retired)
Kaiser Aluminum & Chemical
Corporation
1180 Monticello Road
Lafayette, CA 94549

MEMBERS

Dr. James C. Burrows
Vice President
Charles River Associates
200 Clarendon Street
John Hancock Tower, 43rd Floor
Boston, MA 02116

Dr. Raymond F. Decker
Vice President, Research
Michigan Technological University
Houghton, MI 49931

Mr. Edward J. Dulis
President
Crucible Research Center
Colt Industries Inc.
P.O. Box 88
Pittsburg, PA 15230

Dr. James Economy
Manager, Organic Polymer Research
IBM Corporation
K42-282 Monterey & Cottle Road
San Jose, CA 95114

Dr. Merton C. Flemings
Professor and Chairman
Department of Materials Science
and Engineering
Massachusetts Institute of
Technology
Cambridge, MA 02139

Dr. Brian R.T. Frost
Senior Metallurgist, Materials
Science and Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Dr. Serge Gratch
Director, Material and Chemical
Sciences Laboratory
Research Staff
Ford Motor Company
2000 Rotunda Drive
Dearborn, MI 48121

Dr. Paul J. Jorgensen
Vice President
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

Dr. Bernard H. Kear
Senior Consultant Scientist
Exxon Research & Engineering Co.
Clinton Township
Route 22E
Annadale, NJ 08801

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

Dr. David L. Morrison
President
IIT Research Institute
10 W. 35th St.
Chicago, IL 60616

Dr. David Okrent
Professor of Engineering &
Applied Science
University of California,
Los Angeles
5532 Boelter Hall
Los Angeles, CA 90024

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

Dr. Dennis W. Readey
Professor and Chairman, Department of
Ceramic Engineering
Ohio State University
2041 College Road
Columbus, OH 43210

Dr. James R. Rice
Gordon McKay Professor of
Engineering Sciences and Geophysics
Harvard University
Pierce Hall
Cambridge, MA 02138

Dr. William P. Slichter
Executive Director, Research
Materials Science and
Engineering Division
AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974

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

Dr. Robert P. Wei
Professor of Mechanics
Department of Mechanical Engineering
and Mechanics
Lehigh University
Bethlehem, PA 18015

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

NMAB STAFF

K.M. Zwilsky, Executive Director
S.M. Barkin, Associate Executive
Director

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS			
2a. SECURITY CLASSIFICATION AUTHORITY Department of Defense			3. DISTRIBUTION/AVAILABILITY OF REPORT Cleared for Open Publication			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE						
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NMAB-422			5. MONITORING ORGANIZATION REPORT NUMBER(S)			
6a. NAME OF PERFORMING ORGANIZATION National Materials Advisory Bd. National Research Council		6b. OFFICE SYMBOL (If applicable) NMAB		7a. NAME OF MONITORING ORGANIZATION Department of Defense National Aeronautics and Space Admin.		
6c. ADDRESS (City, State, and ZIP Code) 2101 Constitution Ave., N.W. Washington, D.C. 20418			7b. ADDRESS (City, State, and ZIP Code) Washington, D.C.			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Department of Defense, Nat. Aeronautics & Space Admin.		8b. OFFICE SYMBOL (If applicable) DOD/NASA		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER MDA-903-82-C-0434		
8c. ADDRESS (City, State, and ZIP Code) Washington, D.C. 20301			10. SOURCE OF FUNDING NUMBERS			
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Reliability of Adhesive Bonds Under Severe Environments (Unclassified)						
12. PERSONAL AUTHOR(S) Committee on Reliability of Adhesive Bonds in Severe Environments						
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 2/1/84 TO 7/31/85		14. DATE OF REPORT (Year, Month, Day) December 1, 1984		15. PAGE COUNT 62
16. SUPPLEMENTARY NOTATION						
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)			
FIELD	GROUP	SUB-GROUP	Adhesives Finite element analysis NDE Chemistry Humidity Polymers Creep Interfaces Stress analysis Fatigue Mechanics Surfaces			
19. ABSTRACT (Continue on reverse if necessary and identify by block number)						
<p>A workshop organized by a National Research Council committee and entitled "Reliability of Adhesive Bonds in Severe Environments" was attended by about 100 invited experts. The detailed findings, reported herein, include the recommendation that the federal government spearhead a major effort to overcome the open issues that currently prevent the reliable structural use of adhesive bonding in severe environments. A pervasive comment was that the interdisciplinary nature of the subject requires close interaction of the experts on the chemistry, interphase science, and mechanics of adhesive bonds.</p>						
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS				21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Jerome Persh			22b. TELEPHONE (Include Area Code) (202) 695-0005		22c. OFFICE SYMBOL DOD	

RELIABILITY OF ADHESIVE BONDS UNDER SEVERE ENVIRONMENTS

Report of the Committee on
Reliability of Adhesive Bonds in Severe Environments

NATIONAL MATERIALS ADVISORY BOARD
Commission on Engineering and Technical Systems
National Research Council

Publication NMAB-422
National Academy Press
1984

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

This document has been approved
for public release and sale; its
distribution is unlimited.



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 competencies 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.

This study by the National Materials Advisory Board was conducted under Contract No. MDA 903-82-C-0434 with the Department of Defense and the National Aeronautics and Space Administration.

This report is for sale by the Defense Technical Information Center, Cameron Station, Alexandria, Virginia 22312.

Printed in the United States of America.

ABSTRACT

A workshop organized by a National Research Council committee and entitled "Reliability of Adhesive Bonds in Severe Environments" was attended by about 100 invited experts. The detailed findings include the recommendation that the federal government spearhead a major effort to overcome the issues that currently prevent the reliable structural use of adhesive bonding in severe environments. A pervasive comment was that the interdisciplinary nature of the subject requires close interaction of the experts on the chemistry, interphase science, and mechanics of adhesive bonds.

COMMITTEE ON RELIABILITY OF ADHESIVE BONDS IN SEVERE ENVIRONMENTS

Chairman

SERGE GRATCH, Director, Material and Chemical Sciences Laboratory, Ford Motor Company, Dearborn, Michigan

Members

HALBERT F. BRINSON, Chairman, Center for Adhesion Science, Virginia Polytechnic Institute and State University, Blacksburg

K. LAWRENCE DEVRIES, Professor and Chairman, College of Engineering, University of Utah, Salt Lake City

ALAN N. GENT, Professor, Institute of Polymer Sciences, University of Akron, Ohio

LIENG-HUANG LEE, Senior Scientist, Xerox Corporation, Webster, New York

JAMES S. NOLAND, Manager, Engineered Materials Department, American Cyanamid Co., Stamford, Connecticut

JOHN D. VENABLES, Associate Director, Martin Marietta Laboratories, Baltimore, Maryland

Liaison Representatives

ROBERT REEBER, Army Research Office, Research Triangle Park, North Carolina

STANLEY E. WENTWORTH, Research Chemist, Army Materials and Mechanics Research Center, Watertown, Massachusetts

LEIGHTON H. PEEBLES, JR., Senior Polymer Chemist, Office of Naval Research, Arlington, Virginia

LAWRENCE T. DRZAL, Air Force Wright Aeronautical Laboratory, Wright-Patterson Air Force Base, Ohio

BEN A. WILCOX, Defense Advanced Research Projects Agency, Arlington, Virginia

ROBERT J. REYNIK, Section Head, Metallurgy, Polymers, and Ceramics Section, National Science Foundation, Washington, D.C.

WILLIAM S. JOHNSON, NASA-Langley Research Center, Hampton, Virginia



JEROME PERSH, Staff Specialist, Materials and Structures, Office of Deputy
Under Secretary for Defense for R&E (ET), The Pentagon, Washington, D.C.

NMAB STAFF

JOSEPH R. LANE, Staff Metallurgist

ACKNOWLEDGMENTS

The contributions of the workshop participants are noted with thanks. Major functions were performed by the committee members and liaison representatives. In addition, the following had leadership roles: G. R. Hamed, P. M. Hergenrother, M. F. Kanninen, J. E. McGrath, and J. P. Wightman. These and many others not only contributed during the workshop but also provided important advance input.* The workshop benefited from a program review/workshop held by the Center for Adhesion Science at the Virginia Polytechnic Institute and State University immediately before the NMAB workshop.**

*Two background papers used in the NMAB workshop may be obtained from Dr. K. L. DeVries of the University of Utah and from Dr. L. H. Lee of Xerox Corporation.

**Additional information on this workshop may be obtained from Professor H. F. Brinson, Virginia Polytechnic Institute and State University.

CONTENTS

	Page
1 SUMMARY	1
2 INTRODUCTION	3
3 RECOMMENDATIONS	5
Chemistry	5
Interphases	6
Mechanics	7
4 INTERESTS AND ACTIVITIES OF THE DEPARTMENT OF DEFENSE AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION	9
5 STATE OF THE ART: CHEMISTRY	13
Extreme High Temperatures	13
Extreme Low Temperatures	14
Extreme High Humidity	14
Seawater	14
Other Factors	14
6 STATE OF THE ART: INTERFACES (INTERPHASES)	17
Current Research	19
7 STATE OF THE ART: MECHANICS	21
8 SUMMARY OF DISCUSSION: CHEMISTRY	27
538 to 760°C (1000 to 1400°F) Adhesives	27
288 to 371°C (550 to 700°F) Adhesives	28
177 to 232°C (350 to 450°F) Adhesives	28
23 to 93°C (73 to 200°F) Adhesives	29
-240 to -54°C (-400 to -65°F) Adhesives	29
General Recommendations	29
9 SUMMARY OF DISCUSSION: INTERFACES	31
Surface Preparation	32
Nature of the Interphase	33
Bond Durability	34
10 SUMMARY OF DISCUSSION: MECHANICS	35
Nondestructive Evaluation	36
Test Methods	36
Stress Analysis	37
Finite Element Analysis	37
Failure Mechanisms	37

APPENDIX I Workshop Purpose and Program	39
APPENDIX II Attendees	41
APPENDIX III Overview of Adhesion Science Program Review/Workshop at Virginia Polytechnic Institute and State University	47
APPENDIX IV Biographical Sketches of the Committee	51

PARTICIPANTS at the WORKSHOP



William S. Johnson



John D. Verables



Serge Gratch
Chairman



Paul M. Hergenrother



C. Lynn Mahoney



Lawrence T. Drzal

SUMMARY

Adhesive bonds have several major advantages relative to mechanical fastenings, including potential savings in weight and in manufacturing costs. A recent test of this technology for structural applications, the U.S. Air Force Primary Adhesively Bonded Structure Technology (PABST) program, demonstrated that under favorable conditions such bonds can be quite reliable. Unfortunately, some unresolved issues remain, particularly the degradation of properties of the adhesive joints under hot and/or wet conditions.

This report summarizes the proceedings of a National Materials Advisory Board workshop held to examine the issue of the reliability of adhesive bonds under severe environments.

The main conclusion of the workshop was that adhesive technology has advanced sufficiently so that a concerted effort to resolve those issues left by PABST would have a high probability of success. The workshop participants recommended that the federal government spearhead such a major effort.

Specific research was recommended in the areas of chemistry, interfaces, and mechanics. Some of the recommendations in the area of chemistry included the search for more processable high-temperature adhesives, the search for new synthetic routes to alleviate the evolution of volatiles, research on improved toughening additives, and research aimed at better room-temperature-curing resins.

Some of the recommendations in the area of interfaces (interphases) included research to clarify the general role of adherend topography, search for new adherend surface preparation techniques, research directed at elucidating the requirements for a strong bond, and research on the mechanisms of interphase degradation with time, emphasizing the effects of water, mechanical stress, temperature, and adhesive composition.

Some of the recommendations in the area of mechanics included additional research in the area of nondestructive evaluation (NDE), the

search for mechanical test methods that yield results more directly interpretable in terms of material properties and interphase characteristics, and, in particular, research to determine the relative influences of viscoelasticity (creep), cyclic fatigue, and static strength in severe environments and to characterize interactions between fatigue and creep. To facilitate interlaboratory comparison of results, it was also recommended that standard reference materials be developed and adopted.

Although most of the recommendations were presented under the three separate headings of chemistry, interfaces, and mechanics, the workshop participants stressed that in fact these three areas are closely coupled and the research program must recognize that an adhesive bond is a complex system, requiring an interdisciplinary approach for its optimization.

INTRODUCTION

The potential advantages of adhesive bonds relative to mechanical fastenings such as bolts and rivets are well known. For instance, in a current investigation by the U.S. Army of an all-composite airframe for a helicopter, it has been estimated that the use of adhesive bonding could save about 17 percent in airframe manufacturing costs and 22 percent in weight. Because of these advantages, the use of adhesive bonding for nonstructural applications in military and aerospace products has been growing during the past several years. Extensive experimental studies have been carried out on the structural use of adhesives, such as the U.S. Air Force PABST program. However, even though this program was quite successful, adhesive bonding of structural members has not been accepted by the U.S. military services for various reasons, including the degradation of properties of the adhesive joints under hot and/or wet conditions.

Thus it appears that progress in establishing the reliability of adhesive bonds under severe conditions is the key to allowing the significant potential gains that may come from extensive structural use of adhesive bonds. It seems likely that the technology needed to overcome the remaining deterrents to the structural use of adhesives could be developed soon if appropriate efforts were directed to this objective. Therefore, at the request of the Department of Defense (DOD), the National Materials Advisory Board (NMAB) organized a workshop to establish the technological and scientific requirements for overcoming the limitations of adhesive joints under severe conditions.

The organizing committee, listed on pages v and vi, defined the purpose and scope of the workshop, organized the agenda (see Appendix I), and developed the list of invitees. The response was excellent; the attendance list is shown in Appendix II.

The proceedings of the workshop are summarized in the following chapters. The program started with a review of the needs of the DOD and of the National Aeronautics and Space Administration (NASA). Since the workshop was held immediately after a meeting on adhesion science at

4

Virginia Polytechnic Institute and State University (VPI), it was useful to review next the activities of that meeting (see Appendix III). Brief status reports were then presented for three important subtopics--chemistry, interfaces, and mechanics. Further discussions on each of these subtopics were then carried out by three separate groups. The workshop finally reconvened in plenary session to discuss the findings of the three groups.

It should be noted that, even though it was efficient to break down the subject into the three subtopics of chemistry, interfaces (interphases), and mechanics, in fact, adhesive joints must be treated as a system, and close interaction among the three subtopics is necessary to achieve optimum progress. In particular, close interworking between the experimentalists and the analysts is needed.

Some topics were covered only slightly or not at all during the workshop. These include the effects of scrim on bond performance, flexible adhesives for textiles, and sensitivity to liquids other than water. These omissions were due to a combination of time constraints and interests of participants. It was agreed, however, that some of the omitted topics have considerable importance. An important topic not covered during the workshop is the bonding of elastomers to metals. The Navy has a massive problem with bond failure in sonar transducers, and bond failure has been identified as one of the causes of the Army's tank track pad problem. Another important topic not covered in the workshop is the severe effects expected with chemical decontaminants, in particular the highly corrosive DS2.

The important topic of shelf life was deliberately omitted from consideration, since it was felt that it was dealt with adequately in the report of the NMAB Committee on Room-Temperature-Curing Resin Systems, which was published in March 1984.

Finally, although composite-to-composite bonding was not explicitly stressed during the workshop, this in no way implied lack of recognition of the importance of this area of application. Its importance was evidenced, for instance, by references to the current Army development of an all-composite airframe for a helicopter.

RECOMMENDATIONS

A broad recommendation emerged from the workshop discussions to the effect that, in view of the scientific and technological progress* made since the completion of the PABST program (see p. 9), it is advisable to mount an interdisciplinary effort to go the rest of the way and establish the suitability of adhesive bonding for a range of military and commercial applications requiring high reliability in severe environments. This interdisciplinary effort should involve material science, surface science, mechanics, and process engineering. It should recognize that adhesive bonding must be studied as a complete system, and it should emphasize the specific areas identified in the specific recommendations listed in the sequel. If this is done, the potential benefits are great, the probability of success is high, and the time for a major, concerted effort in this area is now.

More specific recommendations are listed below under the subheadings previously mentioned. Background for these recommendations is given in Chapters 8 through 10 of this report.

CHEMISTRY

- o Synthetic work should be performed to investigate polymer-forming reactions that eliminate evolution of volatiles and provide moisture-resistant polymers with a favorable combination of adhesive properties. This pertains to adhesives for use at all temperature ranges.
- o Studies on model high temperature polymers should be conducted to generate fundamental information on the relationships among structure, cure, physical properties, and mechanical properties.

*Significant progress has been made in new materials (polyimides, polyimide sulfones, polyphenylquinoxalines, etc.), in understanding the mechanism of adhesion failure, and in mechanical modeling of adhesive joints.

- o Basic synthetic work should be directed toward elimination of tenaciously held and toxic solvents, especially for high-temperature polymers.
- o Other known high-temperature polymers should be evaluated as adhesives for short-term, very-high-temperature service 538 to 760°C (1000 to 1400°F).
- o Research should be carried out to improve the processability of high-temperature 288 to 371°C (550 to 700°F) adhesives while retaining good adhesive properties at the temperature of use.
- o New synthetic routes should be investigated to circumvent the need to use toxic monomers.
- o Research should be directed toward toughening the adhesives based on addition-type polyimides, acetylene-terminated phenylquinoxalines, aryloxy-s-triazines (formed from cyanates), and polysulfones for use in the medium-high temperature range 177 to 232°C (350 to 450°F). This may require the synthesis of new toughening agents (e.g., high-temperature elastomers) and investigation of toughening mechanisms at medium-high temperatures.
- o Research should be directed toward investigating crosslinking (curing) mechanisms to obtain fast curing adhesives with no volatile products with a view to optimize curing conditions for adhesive joints.
- o Research should be performed to develop adhesive systems (epoxy replacements, such as acetylene-terminated polymers, polyimides, and aryloxy-s-triazines) that alleviate the shortcomings of conventional epoxy adhesives, for use from room temperature to moderately elevated temperatures [say, to 93°C (200°F)].
- o Research should be performed to develop room-temperature-curing resins with shorter cure time, longer pot time, and better mechanical properties than current room-temperature-curing systems.
- o The desired requirements for low-temperature (below normal room temperature) adhesives should be defined, and priorities for low-temperature applications should be established.
- o Research is encouraged on the exploration of the utility of novel polymers as adhesives, including ordered polymers.

INTERPHASES

- o Further research should be carried out to clarify the general role of adherend topography on bond performance and to optimize it for specific adherends. For example, studies should be made of anodized surfaces to determine the best combination of oxide surface chemistry for a given application. Particular attention should be given to the surface preparation of steel, aluminum, and titanium in view of the importance of these to the armed forces.

- o Alternative adherend surface-preparation techniques should be investigated. For example, can nonaqueous methods be used to anodize and create a mechanically stable and corrosion-resistant surface? Do conversion coatings offer a viable alternative to anodization for titanium and aluminum? Can currently used anodization methods be applied successfully to the new generation of structural materials, such as metal matrix composites and powder metal products?
- o Fundamental research should be directed at quantifying the effect of the adherend on the adhesive and of the adhesive on the adherend. The chemical reactions occurring between polymers and metals at high temperature and their role in the durability of adhesive bonds should be identified.
- o Research should be directed at elucidating the requirements for a strong bond. For example, are chemical forces required or are physical forces sufficient? Are there adequate theoretical concepts to predict adherend-adhesive interaction? What is the role of adhesion promoters and coupling agents?
- o The micromechanics of the interphase should be investigated, taking into account the effects of the presence of materials of radically different composition at distances of only hundreds of nanometers.
- o Techniques should be investigated that might provide in a nondestructive manner a detailed physical and chemical characterization of the interphase. In situ probes may be particularly useful in this connection.
- o Mechanisms of interphase degradation with time should be investigated, with emphasis on the effects of water, mechanical stress, temperature, and adhesive composition. Emphasis should be placed on the approaches discussed on pages 23 and 24. Particular attention should be given to the mechanisms of both water transport and destruction of interfacial bonds through the action of water. Research should also be carried out on the effect of stress on water transport and, in general, on the interaction of the various factors that promote bond degradation.
- o Research should be carried out on the effects of additives and impurities on adhesive bond durability.

MECHANICS

- o Efforts should be made to develop NDE approaches, combining testing and analysis, that would allow identification of good or bad bonds in the absence of obvious physical defects, both as manufactured and in service.
- o Improved nondestructive testing (NDT) techniques should be developed, including automated NDT and techniques suitable for field testing under realistic conditions matching the intended use of the adhesive joint.

- o Improved quality-control methods for manufacturing should be developed.
- o Procedures, to be conducted in conjunction with stress analysis and failure mechanism studies, should be developed to determine critical flaws in critical locations.
- o Mechanical test methods should be developed that yield results more directly interpretable in terms of material properties and interphase characteristics and that are suitable to investigate durability under a variety of loading and environmental conditions. It is particularly important to have input from both the experimentalists and the analysts in the development of these test methods.
- o Mechanical test methods should be developed that require only small quantities of adhesives for the evaluation of novel, experimental materials, which initially may be available only in small amounts.
- o Models should be developed to describe the stress-strain relation throughout an adhesive joint as a function of load, time, temperature, and humidity, with specific attention to the interphase region.
- o The curing process should be investigated and mathematically modeled, with emphasis on the development of residual stresses and defects.
- o Orthotropic material analyses should be made of adhesive joints, especially to account for the performance of scrim cloth and various reinforcements.
- o Finite element analysis (FEA) methods need to be improved to allow handling geometrically nonlinear systems, plasticity, viscoelasticity, three-dimensional conditions, thermal effects, and moisture absorption and migration.
- o Failure mechanisms need to be characterized and a data base developed for several frequently used structural adhesives subject to severe environments.
- o A long-term durability data base should be developed and utilized to verify accelerated characterization test methods.
- o Relative influences of viscoelasticity (creep), cyclic fatigue, and static strength in severe environments should be determined and the interactions between fatigue and creep characterized. What is needed is a fundamentally sound but relatively simple nonlinear three-dimensional viscoelastic-plastic constitutive model for large deformations. Damage development should be a part of the model, and it should be capable of accelerated life (durability) predictions under various severe environments of stress, temperature, moisture, aging, etc.

INTERESTS AND ACTIVITIES OF THE DEPARTMENT OF DEFENSE AND
THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

An adhesive joint must be considered as a system consisting of adherend, metal oxide, primer, adhesive, and other additives. The properties of the joint depend on all parts acting in concert, because any part of the joint can act as a weak boundary. A multidisciplinary approach is necessary to design, fabricate, and test the joint to attain the required reliability and durability necessary for joining of structural components.

The sizes of interest within an adhesive joint vary over seven orders of magnitude, from atomic distances of 10^{-4} micrometers, through the interphase region, latex toughener particles, primer thickness, scrim fabric thickness, surface roughness, voids, and flaws to bondline thicknesses of 10^3 micrometers. Until recently it has not been possible to examine the microstructures in these size ranges. Indeed, it is these size ranges, from the interphase to the matrix microstructure, that control the mechanical properties, toughness, fatigue, and durability of the joint.

The USAF PABST program (Potter 1980) demonstrated that primary adhesively bonded structures could be fabricated. The test component was a portion of the fuselage of the YC-15 aircraft. After 76,230 pressure cycles, equivalent to four lifetimes of fatigue, no fatigue cracks were initiated in the structure as a result of any of the bonding operations. There were no failures attributed to poor surface preparation of the aluminum alloy. There was not one instance of debonding initiated during the test. Furthermore, in spite of the existence of 844 initial bond flaws, there was no significant flaw propagation after the four design lives of durability testing. However, because of uncertainties of surface preparation, fabrication, and nondestructive testing, in addition to the degradation of properties under hot and/or wet conditions, this procedure has not been accepted by the U.S. military services for joining structural aluminum components, in spite of the success of the project and the joining of structural parts by adhesive bonding in European-built commercial aircraft. Large portions of nonstructural parts are joined by adhesive bonding in both military and commercial aircraft manufactured in the United States.

The U.S. Army has an important investigation under way at Bell and at Sikorsky to design an all-composite airframe for a helicopter. Through the use of adhesively bonded composites, it is expected to save some 17 percent in airframe manufacturing costs and a 22 percent airframe weight reduction. This program highlights the need to form reliable composite-to-composite and composite-to-metal joints.

The major source of concern is the required 30-year durability of adhesive joints under conditions of high humidity, high temperature, and sustained loads. Adhesive joints, with few exceptions, do not retain significant strength when subjected to these combined harsh environments. Moisture can enter the joint through the adherend (if it is an organic composite), through the edges of the adhesive, or through cracks and flaws. The moisture lowers the glass transition temperature (T_g), can displace bonds from the adherend interface, and can convert strong metal oxides into bulkier, weaker hydroxides. The effects of moisture on an adhesive joint can be minimized by lowering the permeability of the adhesive, by improving the interfacial bonding, and by using a corrosion inhibitor.

There is a critical need for improved methods of nondestructive inspection. Flaws located near an edge are difficult to detect. One must be able to distinguish between a subcritical and a critical-sized flaw located in a critical area, to detect whether the adherend surface has been properly prepared, and to determine how well "stuck" the joint is (i.e., the quality of the bonded joint). It is also necessary to develop methods for field determination of whether a damaged joint can continue in service, must be repaired, or must be replaced.

Adhesive bonding will be a generally accepted method of joining structural members only after analytical models have been developed that can predict the long-term life of a joint following moisture intrusion, matrix aging, bond displacement, stress relaxation, and damage accumulation.

The needs and interests of DOD and NASA involve the disciplines of mechanics, materials science, and chemistry to achieve the requisite long-term adhesive joints. Mechanical engineering approaches are required to design test methods that relate the experimental observations to the material properties of the components and that are translatable from test specimens to the design of structural components. Of particular need are simple test methods that require a minimum of sample for rapid screening of experimental materials and procedures, yet provide some material properties. Material and surface science approaches are required to characterize the various methods of adherend preparation, to determine the mechanisms of joint failure, and to quantify the composition and properties of the interphase region.

The remaining discussion here of the DOD and NASA needs concentrates on the required properties of adhesives. A wish list of desired properties includes low-temperature and low-pressure cure procedures that can be used in high-temperature applications, the repair of complex parts in the field, the capability of high production rates, and long shelf life of components.

"Low temperature cure" is a misnomer. The desire is to effect adhesive cure without recourse to ovens or heat blankets. The cure temperature within the joint has to be high, however, to attain a high T_g . Typically, for a thermoset, T_g is some 30°C (85°F) above the cure temperature. High bondline temperatures can be obtained by chemical reaction or by high-energy irradiation*.

It is very difficult to maintain cold-storage conditions in the field, and hence the need for a long shelf life for the components. An adhesive system must be processable, the conditions of processing cannot destroy the surface-preparation treatment (a possibility with high-temperature processing requirements), it must be tough, have resistance to a variety of chemicals (fuels, lubricants, de-icers, paint strippers, chemical agents, etc.); be able to withstand temperature excursions within the design limit (high temperature or cryogenic temperature), and be durable and reliable. Any new adhesive system must be designed to minimize adhesive debonding, maximize processability, maximize toughness, and involve many disciplines in the development, fabrication, and certification processes.

A large number of high-temperature adhesive candidates have been developed in DOD, NASA, and university laboratories but have not been fully evaluated. These include but are not limited to LARC-13 and LARC-TPI (U.S. Polymeric), Nadimide terminated polysulfone, polyimide sulfone, partially fluorinated polyimides, polyquinoxalines, and polyphenylquinoxalines. A limited number of high-temperature adhesives and resins are available commercially. These include FM34B (American Cyanamid), Thermid 600 (U.S. Polymeric), Skybond 708 (Monsanto), Isoimide (National Starch), PBI (Acurex), PEEK (ICI), Torlon (Amoco), and Ryton (Phillips). These potential candidates have a number of drawbacks. They are expensive, many require high processing temperatures and pressures, and some thermoplastics can only be used in thin sections because thick sections cool slowly and create large weak crystalline regions.

There is no such item as a generic adhesive. The various steels have different alloy compositions and heat treatments; if grit-blasting is to be avoided as a surface-preparative technique, special physical or chemical techniques have to be developed; the acid or base character of the steel surface will be highly variable; and a variety of conversion coatings are available. Thus each specific joint must be separately tailored for the specified materials and the environmental stresses to which it will be exposed.

The present high-temperature adhesives are generally brittle. New means of improving the toughness must be found. Perhaps the failure mechanism can be modified to allow the joint to craze or form many microcracks without developing a catastrophic macrocrack. Alternatively, it may be possible to develop a thixotropic adhesive, one that will be stiff under normal cyclic fatigue conditions yet will be elastic or plastic under abnormal impact conditions.

*This subject is discussed in National Materials Advisory Board Report NMAB-412 entitled High-Performance Low-Energy-Curing Resins.

The original high-temperature organic materials were absolutely nonprocessable. Processability has been achieved by incorporation of "flexibilizers" or by end-capping oligomers with reactive groups. Unfortunately, these various groups tend to be less stable than the aromatic backbone. Improvements in high-temperature adhesives may be possible by invoking some creative chemistry to look for new synthetic routes to intermediates, new toughening agents or systems, new coupling agents or systems, and new addition-type monomers that can produce thermally stable polymers.

In conclusion, DOD and NASA have a large, growing number of critical opportunities to utilize adhesive joining technology in advanced systems. The reliability of adhesive bonds in a variety of severe environments is the issue that must be resolved if these opportunities are not to be missed. Recent advances in a variety of analytical techniques and methodologies together with new approaches and insights in polymer chemistry have put the solutions within reach. The recommendations summarized in Chapter 3 of this report point the way for DOD and NASA to achieve the desired goals.

REFERENCES

- Potter, D. L. 1980. Primarily Adhesively Bonded Structure Technology (PABST), Service Report AD B 55632. Alexandria, Virginia: Defense Technical Information Service.

STATE OF THE ART: CHEMISTRY

New adhesive materials designed to meet the demands for use in severe environments and for long service life have recently been reviewed [Lee 1984]. The specific environments of concern are extreme high temperatures, extreme low temperatures, extreme high humidity, seawater, and others, including fire and corrosive gases and liquids.

EXTREME HIGH TEMPERATURES

During the past decade, many high-temperature adhesives have been synthesized for aerospace applications. Adhesives for supersonic cruise aircraft must be durable for tens of thousands of cumulative hours at 232°C (500°F), while spacecraft adhesives must withstand hundreds of hours at 316°C (600°F). Missile adhesives must survive for less than 1 minute at temperatures greater than 538°C (1000°F) [Lee 1984]. Besides thermal stability, high-temperature adhesive materials should exhibit processability at approximately 100°C above their T_g . Yet many high-temperature polymers such as polybenzoxazoles (PBOs) or polybenzothiazoles (PBTs) are difficult to process.

For durable bonds, adhesives should be tough. However, many high-temperature adhesives [addition-type polyimides, bismaleimides (BMI), and acetylene-terminated resins] are brittle and need to be toughened by elastomers.

Several processable, thermally stable polymers have been developed, including polyimides (PIs), polyimidesulfone, polyphenylquinoxalines (PPQs), polyimidesulfides hot melt [St. Clair 1984], and triaryl-s-triazine rings (TSTRs) [Hsu and Philipp 1982]. Some promising polymers, such as TSTR and polybenzimidazoles (PBIs), have not been evaluated as structural adhesives. PBIs are suitable for short-term use between 538 and 760°C (1000 to 1400°F).

EXTREME LOW TEMPERATURES

Adhesives for cryogenic engines should maintain their mechanical performance between -184 and -196°C (-300 to -320°F). To meet this need, an experimental composite or a blend of adhesives in a multilayer form has been developed. Apparently work of this type has been carried out at Hughes Aircraft Company, McDonnell Douglas Corporation, or the National Aeronautics and Space Administration-Lewis Research Center, but it is not generally known.

For intermediate low temperatures [e.g., -70°C (-94°F)], several polymers [Schmitt 1983] have been developed for advanced aerospace sealants: cyanosilicones (Product Research Chemical), fluoroalkylarylenesiloxanylene (FASIL, by the Air Force Materials Laboratory), phosphonitrilic fluoroelastomer (PNF, by Firestone Rubber and Tire Company), and flexible polyimides. Future research on intermediate low-temperature adhesives might be pursued along the following lines: (1) cyclic phosphazenes and phosphazene elastomers [Singler et al., in press], (2) polysilarylenesiloxanes [Koide and Lenz 1983], and (3) new fluoroelastomers.

EXTREME HIGH HUMIDITY

Water is a major problem for most adhesive bonds. At present there is no solution for this problem, although some improvements in bond durability have been achieved through the proper selection of a coupling agent or by the application of a corrosion inhibitor, such as nitrilotris-(methylene) phosphonic acid (NTMP) for aluminum [Hardwick et al. 1984]. Water resistance can be improved by the use of fluoropolymers, such as fluoroepoxides [Griffith 1982] or fluoropolyimides. Recently a coordination compound, Volan II, has been shown [Lee 1984] to impart water resistance to a polyethylene and aluminum bond. Three years' water immersion produced no separation of the bond. Thus there is hope for a chemical solution to the water problem.

SEAWATER

Besides bond degradation, the corrosion of metals by salt is another serious problem, and the solution is even more difficult than that for water alone. Researchers developing sonar transducers [R. W. Tinme, private communication, August 1983] have encountered this problem with the elastomer-metal bonds. For aluminum, a surface treatment such as anodizing may improve the resistance of the adhesive joint to salt water [Mindford 1980].

OTHER FACTORS

Fire is not a major concern with adhesives. In addition to additives, phosphorylation has been used to increase the fire resistance for epoxides and polyimides.

For corrosive gases or liquids, no general rule exists. A chemical can be corrosive to a certain type of adhesive and, yet, may be harmless to another.

REFERENCES

- Griffith, J. R. 1982. Epoxy resins containing fluorine. CHEMTECH 12:290.
- Hardwick, D. A., J. J. Ahearn, and J. D. Venables. 1984. Environmental durability of aluminum adhesive joints protected with hydration inhibitors. J. Mat. Sci. 19:223.
- Hsu, L., and W. H. Philipp. 1982. Cyclopolymerization of Aromatic Nitriles and Polymers With Ring-Chain Structures Made Thereby. Presentation at the International Union of Pure and Applied Chemistry Macro Conference, University of Massachusetts, Amherst.
- Koide, N., and R. W. Lenz. 1983. Preparation and properties of poly(silarylene siloxanes). J. Polymer Science 70:91.
- Lee, L. H. 1984. Recent Developments in Adhesive and Sealant Chemistry. To be published in Adhesive Chemistry-Developments and Trends. New York: Plenum Press.
- Mindford, J. D. 1980. Effect of surface preparation of stressed aluminum joints in corrosive saltwater exposure. Adhesives Age 23(10):36.
- Schmitt, G. F., Jr. 1983. Spacecraft, Aircraft, and Missiles: Pushing the Limits of Adhesives, Sealants, and Coatings. Presentation at the Inaugural Symposium for the Case Center for Adhesives, Sealants, and Coatings, Case Western Reserve University, Dayton, Ohio.
- Singler, R. E., G. L. Hagnauer, and R. W. Sicka. In press. Phosphazene Elastomers: Synthesis-Properties-Applications, Part II. To be published in American Chemical Society Symposium Series.
- St. Clair, T. L. 1984. Adhesive Development at NASA-Langley. Presentation at the April 29-May 2, 1984, Program Review/Workshop, Center for Adhesion Science, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

STATE OF THE ART: INTERFACES (INTERPHASES)

Recent studies have demonstrated the importance of surface morphology in determining the integrity of metal-to-polymer bonds [Venables et al. 1979, Kinloch 1980]. In the case of aluminum and titanium, certain etching or anodization pretreatment processes produce oxide films on the metal surfaces that are extremely rough and porous on a microscopic scale. For example, using the high-resolution capabilities of the scanning transmission electron microscope (STEM), it has been observed that the Forest Products Laboratories (FPL) and phosphoric acid anodization (PAA) processes used for preparing aluminum produce surface oxide structures having microporous cells approximately 400 Å wide. For titanium, the chromic acid anodization process developed by Boeing produces an oxide structure that is intermediate between the FPL and PAA oxide on aluminum in both thickness and roughness [Natan and Venables 1983]. Because of their porosity and microscopic roughness, these surfaces mechanically interlock with polymeric coatings, forming much stronger bonds than if the surfaces were smooth. Indeed, evidence has been obtained that this type of bond fails (in the absence of environmental effects) only when the polymer itself fails by viscoelastic deformation [Venables, in press]. In contrast, when the oxide lacks these morphological features and the bond strength is determined solely by chemical forces across the interface, separation can occur rather cleanly at stress levels that may be totally inadequate for structural applications.

The long-term durability of metal-to-polymer bonds is determined to a great extent by the environmental stability (or lack of stability) of the same oxide that is responsible for promoting good initial bond strength (Kinloch and Abbey 1982; Venables, in press; Davis and Venables 1983). For aluminum, moisture intrusion at the bondline causes the oxide to convert to a hydroxide, with accompanying drastic changes in morphology. The resulting hydrated material adheres poorly to the aluminum beneath it, and therefore, once it forms, the overall bond strength may be severely degraded. For titanium, the evidence suggests that its oxides are much more stable than those of aluminum. However, preliminary evidence suggests that in very harsh environments the oxide, which is originally amorphous, undergoes a

polymorphic transformation to anatase; because of volume changes and accompanying morphology changes, this may lead to bond degradation, just as the oxide-to-hydroxide conversion process does for bonds to aluminum [Venables et al. 1979]. This transformation, which is temperature- and humidity-dependent, occurs much more slowly than that of the oxide-to-hydroxide transformation process on aluminum under similar environmental conditions. Nonetheless, since titanium may be used at much higher temperatures than aluminum, it would be of considerable interest to determine the importance of this potential degradation mechanism in the harsher environments in which titanium-to-polymer bonds may be expected to operate.

Although it has been possible to define important factors that govern bond integrity and durability for bonds to aluminum and titanium, no similar concentrated effort appears to have been made to characterize other systems of potential interest to DOD or NASA applications. For example, even though there is considerable interest in bonding parasitic armor or low observable coatings to ship superstructures, Army tanks, etc., very few studies designed to improve the durability of bonds to steel have been made. Some recent investigations, however, have demonstrated that the wedge test, which has been used so successfully to evaluate the durability of aluminum-to-polymer and titanium-to-polymer bonds, is also applicable for steel adherends. In fact, preliminary work using the wedge test has demonstrated significant improvements in bond durability when certain conversion coatings are employed rather than the more conventional method of applying adhesives or primers directly over a grit-blasted steel surface [Trawinski et al. 1984].

Furthermore, it is of interest to note that, for steel, investigators have thus far emphasized surface preparation techniques that remove the oxide (e.g., grit-blasting or etching) rather than techniques that form microporous oxides as on aluminum or titanium. This emphasis undoubtedly arises because oxide coatings on most steels are quite unstable in the presence of moist environments. This great difference in stability between oxides on steel and those on aluminum or titanium therefore suggests that a completely different approach to surface preparation is needed for steel, and a better understanding of the behavior of steel-to-polymer bonds will be needed before consistent and reliable structural bonds can be made to this technologically important material.

Polymer composites are another important class of materials for which adhesive bonding is used as a joining technique. Here, the nature of the material dictates a completely different approach for surface preparation than is used for metals. Currently, in the absence of an understanding of those factors that are important for developing good reliable bonds between composite structures, or between composites and metals, no standard procedures have been developed for optimizing the process. The situation has led to difficulties in which extremely small surface concentrations of contaminants have resulted in debonding at low stress levels. For example, it has been found that 5 percent monolayer coverage of silicone mold release agents (used to allow separation between the composite and the tool on which it is formed) can lead to severe reductions in the strength of composite-to-composite bonds [Matienzo et al. 1983]. Considerable effort is clearly needed to reduce this sensitivity to contaminants.

CURRENT RESEARCH

Within the past several years, there has been a dedicated effort to raise the scientific level of understanding of those factors that govern the stability of adhesive bond interfaces. The power of high-resolution STEMs for revealing the importance of microporous oxides in determining bond integrity has been demonstrated. The importance of sophisticated surface spectroscopy techniques such as X-ray photoelectron spectroscopy (XPS), Auger, Rutherford back scattering (RBS), and Fourier transform infrared (FTIR) to study the stability of surfaces and to investigate means of further improving their stability has also been demonstrated. In addition, new approaches for examining interface stability, such as the surface behavior diagram (SBD), have been specifically developed as tools to aid in examining the interactions between interfaces, the environment to which they are exposed, and inhibitors designed to improve interface stability [Davis and Venables 1983].

REFERENCES

- Davis, G. D., and J. D. Venables. 1983. Surface and Interfacial Analysis in Durability of Structural Adhesives. Ed. by A. J. Kinloch. London, England: Applied Science Publications.
- Kinloch, A. J. 1980. The science of adhesion I. J. Mat. Sci. 15:2141.
- Kinloch, A. J., and W. Abbey. 1982. The Service Performance of Structural Adhesive Joints, p. 181. In Adhesion As a Basis for Joints. Bremen, West Germany.
- Matienzo, L. J., T. K. Shah, and J. D. Venables. 1983. Detection and Transfer of Release Agents in Bonding Processes, p. 604. Proceedings of the 15th National SAMPE Conference, Cincinnati, Ohio.
- Natan, M., and J. D. Venables. 1983. The stability of anodized titanium surfaces in hot water. J. Adhesion 15:125.
- Trawinski, D. L., D. K. McNamara, and J. D. Venables. 1984. Adhesive bonding to conversion coated steel surfaces. SAMPE Quarterly 15(3):6.
- Venables, J. D. 1984. Adhesion and durability of metal/polymer bonds. J. Mat. Sci. (In press).
- Venables, J. D., D. K. McNamara, J. M. Chen, T. S. Sun, and R. L. Hopping. 1979. Oxide morphologies on aluminum prepared for adhesive bonding. Appl. Surf. Sci. 3:88.

STATE OF THE ART: MECHANICS

The stress concentrations associated with mechanical connectors such as bolts and rivets can in part be alleviated by adhesive bonding. However, the stresses are also not uniform for adhesives, and understanding of the mechanisms of adhesive failure is far from complete. The stress and the mechanism of failure are likely to be altered and perhaps complicated by the presence of severe environments. Fortunately, recent advances in experimental techniques and analysis (particularly computer techniques) have provided significant information and insight into both areas. These methods should be amenable to adaptation to explore, predict, and optimize adhesive performance in hostile environments.

In no area of material science is thoughtful care and planning of tests more important than it is for adhesives. Adhesive tests are used for a variety of purposes, including (1) comparing different adhesives, surface preparation methods, or curing techniques; (2) as a quality control check for a batch of adhesives, preparation techniques, effects of aging, etc.; and (3) as a means of determining parameters that can be used to predict the performance of actual practical joints. It is in this third very difficult area that adhesive fracture mechanics holds particular promise.

There has been no dearth of methods proposed and developed to explore adhesives. Some of these have been formalized and published as standards by governmental agencies, the American Society for Testing and Materials (ASTM), etc. Except for a few notable exceptions, these suffer from a common problem; they can be used to predict performance only for practical joints that very nearly duplicate the test specimen's exact geometry. That is, in most standard tests, little if any attention is given to the details of the stress distribution in a joint; rather, results are almost universally given as gross force per unit area. Therefore, these tests yield little if any information on extreme values of the stress or point of failure initiation. There is evidence that the reported "average stresses" may have little direct bearing on the actual failure.

One of the most common and useful types of adhesive test is the single-lap shear test. Not only is it simple and economical to conduct, but

superficially it closely resembles the type of loading to which structural adhesives are often subjected in service. Care must be exercised, however, in interpreting the results and trying to infer strength of practical joints from the given test results. For example, the results of these tests are conventionally given as failure load divided by the area of overlap. Computer analysis shows that the actual stress is far from uniform and becomes much larger than this reported average near the ends of the overlap. Mathematical analyses of stress fields near the bond terminations at sharp corners imply a singularity in the stress field. The nature of the stress field is such that, even without the mathematical simplifications, very large stress concentrations exist in these regions for both elastic and inelastic materials. Perhaps more significantly, the loading of the lap shear joint induces tensile stresses that again become very large near the terminus of overlap. The relative value of the shear and normal stresses depends on details of the adhesive and adherend properties, thicknesses, etc. These tensile stresses are particularly acute for comparatively thin adherends (as generally used in ASTM tests). The evidence is very strong that failure of the joint is more closely related to these crack opening cleavage stresses than to the shear stresses (let alone the reported average shear stress).

Other standard tests that might be broadly classified as either tensile or peel tests suffer from similar problems. The average stresses for loads generally reported tell little of the stress distributions and/or maximum stresses. The nature of these stresses and stress distributions is sensitive to details of adhesive and adherend material properties, geometry, sample or loading frame alignment, etc. A persuasive argument can be made that failure initiation would likely be related more to large local stresses, local stress variations, and/or flaws than it is to average values of a given stress type.

Problems, such as those just outlined, with limiting stress criteria for predicting failure have led engineers and scientists to seek alternative methods that can treat singularities, using parameters obtained from a given test to predict performance of joints with different geometries. The application of the concepts and principles of fracture mechanics to adhesive systems has become quite popular. Fracture mechanics has been quite successful in solving some difficult problems in adhesive failure and has the potential of solving many other adhesive problems. The concepts of fracture mechanics should be helpful in designing tests and experiments to expeditiously explore environmental effects on polymers. Related procedures might help point the way toward designing joints to sustain loads while exposed to hostile environments.

A few observations on adhesive fracture mechanics might be helpful. Inherent in the concepts of fracture mechanics (FM) is the concept that cracks are likely to initiate at flaws or discontinuities. In the case of bonds, additional elastically singular regions can occur at points of abrupt changes in section, geometry modulus, etc. While superficially several FM approaches appear different in concept, such approaches as the energy release rate, stress intensity factor, and J integral can be shown to be essentially equivalent (at least in the elastic case). Considerable evidence exists that adhesive failure is highly dependent on the exact mode of stress at the crack

(debond) tip. Modern computational methods, particularly finite element techniques, have greatly expanded the potential of FM and the geometries, joints, etc., for which it might be used. There is a wealth of FM data, methods, experimental techniques, etc., available on which to base future studies of the durability of adhesives in severe environments. Techniques have been developed to study both static failure (G_I, II, III) and fatigue crack growth.

Tests are needed to determine the critical value of the energy release rate G_c , the critical stress intensity factor K_c , or the critical value of the J integral J_c (perhaps for each of the loading modes). In principle, almost any test could be used. Certain techniques, however, enjoy certain experimental and analytical advantages. A. N. Gent and G. Hamed (1975) have made extensive and fruitful use of peel tests to analyze a wide variety of different fracture mechanical aspects of adhesives. Likewise, the blister test proposed by M. L. Williams (1969) has been adopted by W. B. Jones (1970), G. P. Anderson, B. J. Bennett, and K. L. DeVries (1979), and others to measure G_c for a variety of different adhesive systems. A tapered double cantilever beam developed by E. J. Ripling and S. Mostovoy (1971, 1974), and used by them, Bascom and co-workers (1975), and others, forms the basis of the comparatively new testing standard (ASTM D3433). Johnson and his associates at NASA have been testing and analyzing a variety of different geometries as adhesive fracture mechanics test specimens (Johnson and Mall 1984). Recently, K. N. Liechti and W. G. Knauss developed a biaxial servo-control loading device that can accurately control and independently determine the normal tangential displacement at a crack tip in a bond line with a resolution of approximately 10^{-5} in. (Liechti and Knauss 1982). Such techniques should be helpful in the study of many aspects of fracture mechanics (e.g., the effect of loading mode). It is important to recognize that many other experimental geometries could be used. Fracture mechanics should not be envisioned as a set of rules and/or sample configurations for testing and design. Rather it should be thought of more as a basic philosophy and methodology for approaching testing, design, and evaluation. It may at times be expedient to tailor-make tests for a given system or to design adhesive joints that do not closely resemble the adhesive test in which the adhesive was originally evaluated. In problems of these types, fracture mechanics has inherent potential advantages over other available approaches.

Most adhesives are polymers. While linear elastic analyses might be interesting and informative, a completely satisfactory solution for the stresses, strains, energy release rates, etc., must include considerations of the time- and temperature-dependent properties of the materials. Accordingly, several investigators have made extensive efforts to include viscoelastic effects in their adhesive analyses. Particularly noteworthy are the efforts of M. L. Williams, A. N. Gent and co-workers, W. Knauss, R. A. Schapery, and H. Brinson. Much more work is needed in this area, but these studies clearly demonstrate that in some cases viscoelasticity can be incorporated in the analysis of failure and provide significant insight into the mechanical response of polymers and adhesives.

Without doubt it would be advantageous to have nondestructive methods for detecting flaws such as cracks or regions of debonding along the

bondline. The optimal NDE test would be one in which a measurement could be quickly and easily made that does not damage the joint(s) or structure and yields results that can be directly related to the strength of the bond. A great many experimental techniques have been brought to bear on this problem, including (1) for adherend surface inspection, the contact angle, surface potential difference, and surface impedance, and (2) for NDE of the complete bond, capacitance measurement; radiographic (X-ray, Y-ray, neutron, etc.) inspection; thermal inspection methods, including variations in thermal conductivity, thermal emissivity, thermal capacity, or local differences in thermal expansion; acoustic emission; acoustic inspection, such as the coin tap and its related instrumental counterparts like the Fokker Bond Tester Type I; ultrasonic techniques, including through-transmission, pulse echo techniques, resonance techniques, and spectral analysis; and holographic interference.

The current state of the art for locating and determining the size of flaws is quite good and is progressing rapidly. The ability to predict the effect of these flaws on strength, debonding load, etc., is not as well developed. For a few selected adhesives and joint designs there have been some rather impressive correlations between NDE measurements and bond strength, but more study is needed before generally applicable techniques and models will be available. Most of the techniques listed here should be adaptable to the investigation of bonds intended for use in severe environments.

Acoustic emission (AE) shows promise of providing a measure of the "onset" and "accumulation" of damage. G. P. Anderson of Morton Thiokol reports, for example, that in studies of debonding of a system tunnel that runs the entire length of the space shuttle, AE techniques readily detect damage at loads of 40 to 60 percent of those for which there is any visual evidence of damage (DeVries and Anderson 1979; private communication between K. L. DeVries, University of Utah and G. P. Anderson, Morton Thiokol, April 1984).

In conclusion, a number of thermally and environmentally stable polymers have recently become available. It seems probable that some of these can be developed into adhesives for use in severe environments. It appears that the time is ripe to exploit some of this potential. Fortunately, experimental techniques, analytical methods, and computer techniques are available that can be adapted for characterizing these adhesives and designing for them.

Experimental techniques and analysis based on the principles of fracture mechanics should be much more informative than measurements of the effect of various hostile environments on gross joint strength. With care, well-planned experiments and analysis should provide insight into the effect of these agents on more fundamental parameters, such as the adhesive or cohesive fracture energies, adhesive and adherend moduli, interfacial degradation, corrosion, or other structural changes. Models based on an understanding of the basic mechanisms responsible for behavior should provide more reliable predictions of long-term performance.

REFERENCES

- Anderson, G. P., S. J. Bennett, and K. L. DeVries. 1979. Analysis and Testing of Adhesive Bonds. New York: Academic Press.
- Bascom, W. B., R. L. Cottingham, R. L. Jones, and P. Peyser. 1975. Fracture of epoxy and elastomer-modified epoxy polymers in bulk and as adhesives. J. of Appl. Poly. Sci. 19:2545.
- DeVries, K. L., and G. P. Anderson. 1979. Analysis of Design of Adhesive Bonds. Lecture Series 102, Bonded Joints and Preparation for Bonding. AGARD-LS-102. NATO.
- Gent, A. N., and G. Hamed. 1975. Peel mechanics. J. of Adhesion 1:91.
- Johnson, W. S., and S. Mall. 1984. A Fracture Mechanics Approach for designing bonded joints. NASA Technical Memorandum 85694. Washington, D.C.: National Aeronautics and Space Administration.
- Jones, W. B. 1970. Cohesive and Adhesive Polymer Fracture Investigation. Ph.D. Dissertation, University of Utah.
- Liechti, K. N., and W. G. Knauss. 1982. Crack propagation at material interfaces: No. I experiment tech. to determine crack profiles. Experimental Mechanics 22:262.
- Mostovoy, S., and E. J. Ripling. 1971. J. of Appl. Poly. Sci. 15:641.
- Mostovoy, S., and E. J. Ripling. 1974. Fracturing Characteristics of Adhesive Joints. Final Report under contract #N00019-73-C-0163. Watertown, Massachusetts: Materials Research Laboratory, Army Materials and Mechanics Research Center.
- Williams, M. L. 1969. Continuum interpretation for fracture adhesion. J. of Appl. Poly. Sci. 13:29.

SUMMARY OF DISCUSSION: CHEMISTRY

The adhesive chemistry discussion focused on aerospace applications of structural adhesives for use in severe environments as implied by the needs of the Army, Air Force, Navy, and NASA. It was recognized that each of the services has requirements for adhesives for use in unique environments besides structural applications. Limited time, however, restricted the discussion primarily to structural adhesives. Severe environments include use under various combinations of temperature, time, stress, moisture, chemical and electrical action, and irradiation. Although the discussion centered on the chemistry of adhesives, it was well recognized that there are many important parameters to be considered in a bonded joint. These include items such as adherend, surface treatment, interface, primer, carrier, filler, adhesive tape character, cure conditions, joint design, stress loads, environment, and failure mode. Thus, a comprehensive fundamental program on adhesives must encompass chemistry, mechanics, and interfaces.

The requirements for adhesives for use in severe environments were categorized with regard to maximum use temperatures and use times at those temperatures as shown in the following table:

<u>Use Temperature, °C (°F)</u>	<u>Use Time</u>
538 to 760 (1000 to 1400)	Seconds to minutes
288 to 371 (550 to 700)	Hundreds of hours
177 to 232 (350 to 450)	Thousands of hours
23 to 93 (73 to 200)	Tens of thousands of hours
-240 to -54 (-400 to -65)	Seconds to thousands of hours

Obviously, other environmental factors are involved, but these are difficult to define since each application has its own specific requirements.

538 TO 760°C (1000 TO 1400°F) ADHESIVES

Adhesives performing in the 538 to 760°C temperature range are needed for use in missiles and advanced weapon systems. Two families of aromatic heterocyclic polymers, PBIs and polyquinoxalines (PQs), have demonstrated

usable strength in the 538 to 760°C range. PQs are unavailable and must be custom synthesized. PBI is commercially available in limited quantities. PQ can be processed at high temperature (e.g., 371 to 399°C under 200-psi pressure) with low volatile content, whereas considerable volatiles are evolved during the fabrication of bonded areas with PBI.

The adhesive chemistry group recommends that other known high-temperature polymers be evaluated as adhesives for use in the 538 to 760°C temperature range. In addition, research should be directed toward the development of new synthetic routes leading to PQ, PBI, and other ultra-high-temperature polymers that alleviate the evolution of condensation volatiles and tenaciously held residual solvent.

288 TO 371°C (550 TO 700°F) ADHESIVES

Adhesives performing in the 288 to 371°C temperature range are needed for structural use in advanced aircraft and space vehicles. Several different families of aromatic heterocyclic polymers such as PQs, PBIs, PIs, and PPQs have been evaluated for use in this temperature range. PQs have displayed good adhesive strength retention at 371°C after 50 hours at 371°C in air, whereas PPQs exhibited good performance at 316°C after 500 hours at 316°C in air. Commercial PI adhesives are available, but large quantities of volatiles are evolved during fabrication. There are several problems associated with these experimental linear amorphous polymers. High temperatures and high pressures (temperatures >316°C and pressures >100 psi) are required in processing. Many of these thermoplastics creep under load at elevated temperatures and, when under stress, exhibit solvent sensitivity. Most of these polymers are made using toxic monomers (e.g., aromatic amines).

Research should be directed toward improving the processability of these polymers while retaining their good adhesive properties at elevated temperatures. Research should also be undertaken to develop new synthetic routes that circumvent volatile evolution and the use of toxic monomers. Other known polymers should be evaluated as adhesives for use in the 288 to 371°C temperature range.

177 TO 232°C (350 TO 450°F) ADHESIVES

Adhesives performing in the 177 to 232°C range are needed primarily for structural use in military airplanes, high-speed advanced commercial aircraft, conventional commercial aircraft (engine area), and advanced helicopters. Several different families of polymers such as PQs, PBIs, PIs, PPQs, addition-type PIs, acetylene-terminated phenylquinoxalines (ATPQs), and other acetylene-terminated polymers (ATPs) have shown promising performance as adhesives in the 177 to 232°C range. A linear amorphous PI has shown no loss in lap shear strength at 232°C after aging for 30,000 hours at 232°C in air. The linear amorphous thermoplastic polymers (e.g., PQ, PI, and PPQ) require processing temperatures about 100°C higher than their glass transition temperatures. The addition-type PIs as well as the ATPQs and ATPs are generally brittle.

The adhesive chemistry group recommends that research be directed toward toughening the addition-type PIs, ATPQs, and ATPs either by incorporating toughening phases within the polymer chain via monomers or by the addition of toughening agents (elastomeric materials) that will perform in the 177 to 232°C range. This may necessitate the synthesis of specific toughening agents (e.g., high-temperature elastomers). In addition, research should be undertaken to determine the mechanism of toughening of these high-temperature adhesives.

23 TO 93°C (73 TO 200°F) ADHESIVES

The most popular structural adhesives for the 23 to 93°C range are epoxies, particularly rubber-toughened (RT) epoxies. In general, these materials perform well. However, there are specific applications where debonding occurs. For example, debonding of the sandwich-constructed Army field shelters is a major problem in hot and moist or extremely cold climates. A variety of epoxies are used as RT curing resins for field and depot repair of damaged components. Problems associated with epoxies include moisture sensitivity, long cure time, and limited shelf life.

The adhesive chemistry group recommends research to develop adhesive systems (epoxy replacements such as ATPs or cyanates) that alleviate the shortcomings of conventional epoxy adhesives. In addition, research should also be undertaken to develop a better RT curing resin with shorter cure time, longer out time, and better mechanical properties than current RT curing systems.

-240 TO -54°C (-400 TO -65°F) ADHESIVES

The need for adhesives for use in a cold environment is recognized, however, the state of the art, problems, and needs for adhesives for use in cold conditions was beyond the scope of the workshop.

GENERAL RECOMMENDATIONS

It is recommended that research be undertaken in the following areas:

1. Synthetic research should investigate polymer-forming reactions that eliminate evolution of volatiles and provide moisture-resistant polymers with a favorable combination of adhesive properties. This pertains to adhesives for all of the temperature-use ranges.
2. Studies on a model system (e.g., ATPs) should be conducted to generate fundamental information on the relationships among structure, cure, physical properties, and mechanical properties.
3. Basic synthetic work should be directed toward the development of water-based adhesive systems, especially for high-temperature polymers, to eliminate tenaciously held and toxic solvents.

SUMMARY OF DISCUSSION: INTERFACES

In any adhesive bond, the interface between adhesive and adherend is an integral functioning component of the joint. Interactions between the adhesive and the adherend at the interface occur that are a necessary precursor to satisfactory adhesive joint performance. This interface must transfer loads between adhesive and adherend during the useful lifetime of the adhesively bonded joint without substantial degradation.

Recommendations that address adhesive bond performance in severe environments require that the interface and its role in bond reliability be addressed. The collective knowledge of the scientific and technical community suggests that any study of the interface begins with a realization of the fact that the traditional picture of the two-dimensional nature of the interface is outdated. Realistically, the interface is a three-dimensional "interphase" (Figure 1) extending from some point in the adherend where the local properties begin to change from the bulk

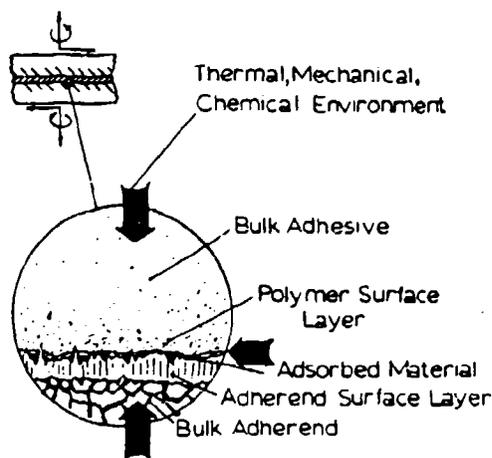


Figure 1 Interphase.



properties, through the "interface," and into the adhesive where the local properties approach the bulk properties. Depending on the actual adhesive-adherend system, this interphase can extend from a few to a few hundred nanometers. On the adherend side it includes morphological alterations in the adherend near the surface as well as oxides either deliberately constructed or native to the adherend surface. This oxide can vary in porosity and microstructure from the regular columnar anodized type to natural oxides having a disordered morphology. Adsorbed gases may be present on the oxide surface, giving rise to unfavorable thermodynamic wetting of the surface by the adhesive, and/or these volatile species may be the source of voids in the formed adhesive bond. The polymeric adhesive is likewise affected by the presence of the adherend surface. Certain nonreactive adhesive components may be free to diffuse to the oxide surface in higher concentration than in the bulk. Primers used to protect the surface prepared for bonding can create structurally different regions and may contain corrosion-inhibiting components present in particulate forms. The polymeric network may also be altered in the region near the adherend surface, giving rise to a material different in composition and mechanical properties.

This interphase is formed under the dynamic conditions existing during the processing of the adhesive bond. It is an integral part of the formed bond and is subject to the mechanical, chemical, and thermal environment experienced by the adhesive joint during its useful lifetime.

Acceptance of this "interphase" as a working model of the actual joint interface serves as a framework for the systematic enumeration of the research needs that must be addressed to make the adhesive interface a functioning component of an adhesive bond and not a limiting factor to its performance in severe environments.

SURFACE PREPARATION

The logical beginning of the discussion of the interface is the surface preparation of the adherend. Because this step occurs before actual bond formation, characterization of the surface is straightforward. A spectrum of surface and bulk analytical techniques currently available can be used to characterize the adherend surface.

Further research is required mainly to address certain generic questions that are applicable to a greater or lesser degree in all classes of potential adherends (i.e., metals, ceramics, and polymers), namely, what is the effect of adherend topography on bond performance, and can alternative surface preparation techniques be used for adherend preparation?

It is generally agreed that some form of topographical alteration in an adherend surface is necessary to achieve optimum bond performance. Traditionally this has meant electrochemical anodization for metals and surface roughening for nonmetals. Research is required to identify the topographical features that enhance adhesive joint performance and permanence. For example, what is the proper combination of oxide thickness, pore size, wall thickness, and oxide surface chemistry for a given application? Can nonaqueous methods be used to anodize and create a

mechanically stable and corrosion-resistant surface? Do conversion coatings offer a viable alternative to anodization methods for the generation of a mechanically, chemically, and thermally durable oxide? In a more short-term vein, can the currently used anodization methods be applied successfully to the new generation of structural materials, such as metal matrix composites, adherends prepared with powder metallurgical techniques, lithium alloy aluminums, titanium alloys for high-temperature applications, and structural steels?

NATURE OF THE INTERPHASE

Once the adherend surface has been prepared, actual formation of the bond occurs. During the application of temperature and pressure the adhesive becomes fluid and the interface forms. Fundamental research must be directed at quantifying the effect of the adherend on the adhesive and the adhesive on the adherend. Isolated investigations of the adhesive are not directly relatable to the performance of the adhesive in the bond. Specifically, what is the gradient of properties thought to exist in the adhesive, and how can it be quantified? Are chemical forces necessary for optimum adhesion or are physical forces sufficient? Can concepts such as the acid-base interaction approach or the use of surface-behavior diagrams be utilized to predict polymer-substrate interaction? How do adhesion promoters and/or coupling agents function structurally in the joint and as an enhancement to bond durability?

The corollary to these materials questions is, from a micromechanics viewpoint, what effect can materials of differing composition existing in an interphase region only a few hundred nanometers thick have on the mechanical, chemical, and thermal responses of the adhesive joint? Although complete characterization of the interphase is not available, investigation of the micromechanics of a region of this size is highly desirable.

Implicit in this need to identify the nature of the interphase is the ability to characterize the interphase as it exists in the joint. Some analytical characterization techniques exist that can provide the atomic and molecular information required to characterize the interphase. These, however, usually require the destructive separation of the joint for success. It is necessary to have the ability to interrogate nondestructively the interphase as it exists in the joint. Some new approaches to this problem appear to have potential and warrant further development.

A partial listing of these techniques would include neutron beam techniques, Rutherford backscattering, polarization modulation FTIR, nuclear magnetic resonance (NMR) tomography, and ultrasonic Rayleigh waves. Other analytical techniques not capable of in situ characterization but offering information for potential interphase characterization are internal reflection spectroscopy, ultraviolet visible labeling, and ultramicrotomy in conjunction with analytical electron microscopy.

Significant accomplishments in this area not only offer the possibility of providing the necessary information for materials characterization of the

interphase but also offer the hope of leading to a nondestructive method for inspecting and evaluating the adhesive joint during its lifetime.

BOND DURABILITY

The events that lead to bond formation occur within a very short time span. The functioning of the adhesive joint in a severe environment is expected to be on the order of years. Mechanisms of degradation with long time constants can be very important to a bond's durability in an adhesive joint. Research needs in this area involve kinetic and thermodynamic phenomena. Four factors--water, stress, temperature, and adhesive composition--must be addressed.

The transport of water to the interface must be considered on two levels. First, the question of the importance of interfacial versus bulk diffusion of water must be addressed; second, at the molecular level are chemical factors or morphological considerations important in water transport. Of equal importance is the effect of water on the destruction of interfacial bonds. Identification of these mechanisms offers the possibility of creating a moisture-insensitive interface through proper materials selection and alteration of the adhesive-adherend combination. The effect of mechanical stress on the durability of an adhesive joint needs to be explored further. Research should explore the change in moisture transport with different stress levels and types. A better understanding of the mechanics of load transfer through the interphase region is required in order to optimize the interphase structurally. Elevated temperatures allow degradation mechanisms to operate that might not be favorable under ambient conditions. The synergism between water, stress, and temperature and its effect on the kinetics of interfacial degradation must be emphasized if a viable predictive model of long-term interfacial bond durability is to be developed.

Finally, the components of the adhesive itself must be investigated further to determine their effect on bond durability. This investigation should include the effects of impurities, of processing additives, and of fillers.

SUMMARY OF DISCUSSION: MECHANICS

An interdisciplinary approach to adhesives research is gaining wide acceptance. This approach requires researchers from the fields of chemistry, materials science, and mechanics to work closely together to develop a basic understanding of the adhesion process. However, there exist many disciplines within the mechanics area that must work hand-in-hand to make effective progress. Nondestructive testing, stress analysis, finite element analysis, material modeling, experimental testing, and structural design are a few of these specialized disciplines.

Within the mechanics area there are two research goals: design and basic understanding. Although these two goals are not in conflict, they do, in certain problem areas, require two somewhat different approaches to the problem. Basically, design research is oriented toward the application of adhesives to structures. This approach recognizes that every aspect of the adhesive problem cannot be incorporated into the design criteria because of the need to keep the design criteria as simple as possible. It is hoped that the major concerns will be accounted for and that a safety factor will be applied to cover the unknown. The design approach would, in general, consider the adhesive joint to be a single system and would be concerned with the response of that system as a whole. In contrast, the basic understanding approach is more scientific in nature, with emphasis placed on developing a complete understanding of each component of an adhesive joint and their interactions. However, such research is not easy; indeed, much of it, although very important, must be considered long-term.

As one outcome, the workshop participants identified the need for standard reference materials; these do not necessarily have to be chemically well-characterized materials, as long as the properties are reproducible. Such materials would allow intercomparison of the results of different laboratories and clearer interpretation of the effects of design and application variables. It was agreed that this goal is attainable, even though care must be used to minimize the effect of aging during adhesive storage.

The following sections address five areas of general mechanics research: nondestructive evaluation, test methods, stress analysis, finite element analysis, and failure mechanics. Each section contains a short descriptive paragraph followed by a mention of specific research needs.

NONDESTRUCTIVE EVALUATION

The current state of the art in NDT of adhesive joints is such that most physical defects such as porosity, debonding, and voids can be found in a laboratory environment. The detection and interpretation of defects may require more than one test technique. The size of the largest flaw not found must be used with a fracture mechanics approach to determine critical loads as a function of defect location. A good NDE program requires the combination of NDT to find defects and a physical mathematical model (e.g., fracture mechanics) to evaluate the significance. Therefore, NDT is used for quality control as well as to establish input data for design.

At least five topics in the area of design were identified as calling for research. A long-standing problem is establishing the quality (strength) of a bond. Developing an NDE procedure to determine good or bad bonds should be regarded as potentially long-term. More recent interest has developed in automating NDT techniques for application to large-scale manufacturing and to adapting NDT techniques to field inspection. Procedures for determining critical flaws must be done in conjunction with stress analysis, considering possible failure mechanisms. Similarly, work is also needed on the development of methods of quality control during manufacturing.

Two topics in the area of basic understanding were emphasized as needing research. These were NDE techniques to study material degradation and damage growth in adhesive joints, and the development of methods to evaluate surfaces and adhesives separately prior to bonding.

TEST METHODS

Many specimens and test methods for evaluating adhesives already exist. In spite of this, there is a severe shortage of reliable basic material property data such as G , E , ν , G_{Ic} , and G_{IIc} . Furthermore, recent developments in stress analysis techniques (i.e., finite element methods) have revealed that popular specimens, such as the single-lap shear, are quite complex and their results very misleading when used in a traditional manner. It is important for experimentalists and stress analysts to work together to design new test methods and specimens and to reevaluate current testing procedures.

New test methods and specimens are needed to measure specific basic material properties. In addition, durability tests on adhesive joints, meaning resistance to fatigue, creep, exposure, etc., need to be developed. The specimens must be well analyzed and understood. They must be suited for environmental testing and, if possible, should be representative of an application. Also needed are new, small test specimen designs for adhesive material evaluation and screening.

STRESS ANALYSIS

Currently, accurate stress analysis of adhesive joints is limited by the lack of reliable data on materials properties for the adhesive, the interphase region, and, in some cases, the adherends. Adhesive properties are, for the most part, time-, temperature-, and humidity-dependent. Thus the environment as well as the load plays a significant role in stress analysis.

For design research, the stress analysis and accompanying failure criteria must be kept simple and efficient yet be accurate enough to be covered by a reasonable factor of safety. The basic understanding approach requires a more exacting knowledge of the material properties and stress distributions throughout the joint. When a given aspect of the adhesive joint (e.g., viscoelasticity) is found to have a significant effect on the joint stress distribution, it must be integrated into the design procedure.

One of our deficiencies is the lack of a model to describe the stress-strain relation throughout the joint as a function of load, time, temperature, and humidity. It is recognized that such a model would be material dependent. The use of a scrim cloth effectively turns the adhesive into a composite. It would be desirable to have the capability of treating the adhesive as an orthotropic material. It would be desirable, also, to treat through stress analysis the relationship of neat adhesive properties to joint properties. Finally, our basic understanding of the effect of changes occurring during cure on residual stress is inadequate.

FINITE ELEMENT ANALYSIS

Finite element analysis (FEA) is a specific type of stress analysis. However, FEA has become a discipline of its own because of the sophistication involved with present numerical analysis techniques. The problems that can be accurately solved with FEA are virtually limitless compared to the number of closed-form solutions or strength-of-materials approximations. As powerful as FEA is, the results are only as good as the modeling of the material behavior and the geometric conditions. A number of excellent FEA computer programs have recently been developed specifically for analysis of bonded joints and are currently undergoing evaluation. However, none of these codes is as flexible as might be desired.

Research would be assisted if flexible programs that can handle geometric nonlinear analysis, plasticity, viscoelasticity, 2-D or 3-D analysis, thermal effects, resin and interphase degradation, and moisture absorption and migration were available. These programs should be as cost-efficient as possible without sacrificing accuracy. The FEA must be able to model realistic material behavior.

FAILURE MECHANISMS

To design an efficient, durable adhesively bonded structure, maximum design stresses must be established. Such stresses are those associated with failure, for example, by long-term creep rupture, cyclic fatigue, or

static failure due to material degradation. Potential failure mechanisms and their associated stress and environmental dependence must be characterized for each adhesive prior to application. Fracture mechanics has been demonstrated to be a viable tool for characterizing and predicting static strength and cyclic debonding of adhesive joints containing initial debonding. Several viable nonlinear viscoelastic models exist for the prediction of long-term creep rupture. There is general agreement that emphasis should be placed on defining the threshold region for fatigue damage and creep rupture and then using these data as upper design limits.

The failure mechanisms of several frequently used structural adhesives when subjected to severe environments needs to be established. Such determinations will also permit the development of an experimental data base, which is needed. One use of a long-time durability data base is to verify accelerated characterization test methods. The testing mentioned above will help define the relative influences of viscoelasticity (creep), cyclic fatigue, and static loading in severe environments, and also to characterize fatigue and creep interactions.

APPENDIX I

WORKSHOP PURPOSE AND PROGRAM (From Program Announcement)

PURPOSE AND SCOPE

The broad field of polymer science and engineering offers many opportunities for major advances. There are many products that fall short of military and NASA requirements. In the case of polymeric adhesives, there are both problems and promise. Some restricting factors are the limited ability to withstand high temperatures (above 350°C), cryogenic temperatures, and cyclic loading. The ability to detect "weak" bonds and to predict service life are both very poor, and technology development is needed before more structural uses develop. Interesting new polymers have recently been developed, and understanding of surface science is improved. Therefore it appears that major advances in adhesive joining technology are possible that can lead to useful and needed products. Adhesive formulations alone are not at issue. As reflected in the workshop program, advances in evaluation, stress analysis, and interface reactions can all lead to progress in the field. The unclassified workshop will highlight some of the opportunities to permit the committee to make recommendations to DOD and NASA as to promising research directions.

AGENDA

May 3, 1984

Lecture Room

9:00	Welcome Introduction	Serge Gratch
9:30	Interests and Activities of the Department of Defense and the National Aeronautics and Space Administration	Leighton Peebles
10:15	Break	
10:30	Overview of Virginia Polytechnic Institute and State University Program Review/Workshop	Halbert Brinson Melvin Kanninen J. E. McGrath
11:30	Lunch	

East Auditorium, State Department**Summary of Research Needs
(Stanley Wentworth, Chairman)**

1:15	Chemistry	Lieng-Huang Lee
2:00	Interfaces	John Venables
2:45	Mechanics	K. Lawrence DeVries
3:30	Break	
3:45	Discussion	
4:30	Adjourn	

May 4, 1984

NAS Rooms 080, 180, 280**Simultaneous Discussion Sessions**

9:00- 11:45	Mechanics (inspection, accelerated testing, stress, stress analysis, failure analysis) Room 280	Gary Hamed Discussion Leader
	Interfaces (surface preparation, metal reactions, water penetration) Room 180	James Wightman, Discussion Leader
	Chemistry (new materials, extreme tempera- ture formulations, low-temperature curing) Room 080	James Noland, Discussion Leader
11:45	Lunch	

Lecture Room**Reports of Discussion Sessions
(Serge Gratch, Chairman)**

1:00	Chemistry	Paul Hergenrother
1:45	Interfaces	Lawrence Drzal
2:30	Mechanics	William S. Johnson
3:15	Close of Workshop	

APPENDIX II

ATTENDEES

Workshop on
Reliability of Adhesive Bonds Under Severe Environments

May 3-4, 1984

Randall E. Adam
Manager, Polymer Research Group
3M Center
3M Company
St. Paul, MN 55144

Pedro Albrecht
Department of Civil Engineering
College of Engineering
Room 0215, Surge Facility
University of Maryland
College Park, MD 20742

Garron P. Anderson
Morton Thiokol Inc.
Wasatch Division
P.O. Box 524, M/S 287
Brigham City, UT 84302

Clifford S. Astill
National Science Foundation
Engineering Directorate
1800 G. St., N.W.
Washington, D.C. 20550

Johnathan Awerbuch
Department of Mechanical Engineering
Drexel University
Philadelphia, PA 19104

F. J. Boerio
Dept. of Materials Science
University of Cincinnati
Cincinnati, OH 45221

D. A. Bolstad
Materials Engineering Section Chief
Department 3516
P.O. Box 29304
Martin Marietta
New Orleans, LA 29304

Halbert F. Brinson
Professor
Virginia Polytechnic Institute
and University
Engineering Science and Mechanics
Dept.
Blacksburg, VA 24061

Stanley Brown
Code 60622
Naval Air Development Center
Warrminster, PA 18974

Albert H. Cardon
Fac. d. Toegepaste
Wetenschappen
Vrije Universiteit Brussel
Pleinlaan, 2
B-1050 Brussel
BELGIUM

K. Lawrence DeVries
 Professor and Chairman
 College of Engineering, M and IE
 University of Utah
 Salt Lake City, UT 84112

B. Boro Djordjevic
 Research Scientist, Nondestructive
 Evaluation
 Martin Marietta Laboratories
 1450 S. Rolling Rd.
 Baltimore, MD 21227

Lawrence T. Drzal
 Air Force Wright Aeronautical
 Laboratory
 AFWAL/MLBM
 Wright-Patterson AFB,
 OH 45433

D. W. Dwight
 Materials Engineering Dept.
 Virginia Polytechnic Inst.
 and State University
 Blacksburg, VA 24061

Semih Erhan
 Director Research
 Department of Dental Medicine
 Albert Einstein Medical Center
 York and Tabor Rds.
 Philadelphia, PA 19141

Frederick M. Fowkes
 Department of Chemistry
 Lehigh University
 Bethlehem, PA 18015

Alan N. Gent
 Professor
 Institute of Polymer Sciences
 University of Akron
 Akron, OH 44325

Serge Gratch
 Director, Material and Chemical
 Sciences Laboratory
 Research Staff
 Ford Motor Company
 2000 Rotunda Drive
 Dearborn, MI 48121

Gary R. Hamed
 University of Akron
 Institute of Polymer Science
 Akron, OH 44325

S. Richard Hartshorn
 3M Company
 3M Center, 209-1N-18
 St. Paul, MN 55144

Sarah Willis Hartwell
 R.J.R. Archer, Inc.
 Bowman Gray Development Center
 Reynolds Blvd.
 Winston-Salem, NC 27102

Richard W. Helmke
 Chief, Concepts and Composites Branch
 Engineer Support Laboratory
 Research and Development Center
 ATTN: STRBE-NBC
 Ft. Belvoir, VA 22060

E. G. Henneke
 Department of Engineering Science
 and Mechanics, 218 Norris Hall
 Virginia Polytechnic Institute
 and State University
 Blacksburg, VA 24061

Paul M. Hergenrother
 Senior Polymer Scientist
 Materials Division
 Mail Stop 226
 NASA Langley Research Center
 Hampton, VA 23665

Brian Hornbeck
 Cmdr. U.S. Army
 Ft. Belvoir R&D Center
 Attn: STRBE-NBC
 Ft. Belvoir, VA 22060

Li-Chen Hsu
 NASA-Lewis Research Center
 21000 Brookpark Rd.
 Cleveland, OH 44135
 (216) 433-4000, ext. 6602

Donald Hunston
 Polymer Science and
 Standards Div.
 National Bureau of Standards
 Washington, D.C. 20234

Hatsuo Ishida
 School of Engineering
 Department of Macromolecular Science
 Case Western Reserve University
 Cleveland, OH 44106

W. Steve Johnson
 Mail Stop 188E
 NASA-Langley Research Center
 Hampton, VA 23665

William B. Jones
 Department of Mechanical Engineering
 Texas Tech University
 Box 4289
 Lubbock, TX 79409

Melvin F. Kanninen
 Southwest Research Institute
 P.O. Drawer 28510
 San Antonio, TX 78284

R. Kerber
 Defense Advanced Research Projects
 Agency
 Department of Defense
 1400 Wilson Blvd.
 Arlington, VA 22209

J. M. Klarquist
 Shell Development Co.
 One Shell Plaza
 Houston, TX 77001

W. G. Knauss
 Graduate Aeronautical Laboratories
 105-50
 California Institute of Technology
 Pasadena, CA 91125

Irvin M. Krieger
 Department of Chemistry
 Case Western Reserve University
 Cleveland, OH 44106

Gordon P. Krueger
 Institute of Wood Research
 Michigan Technological University
 Houghton, MI 49931

James A. Koutsky
 Department of Chemical Engineering
 University of Wisconsin
 Madison, WI 53706

S. S. Labana
 Manager, Polymer Science Department
 SRLB-S3086
 Ford Motor Co.
 P.O. Box 2053
 Dearborn, MI 48121

Joseph R. Lane
 Staff Metallurgist
 National Materials Advisory Board
 National Academy of Sciences
 2101 Constitution Ave., N.W.
 Washington, D.C. 20418

David F. Lawson
 Firestone Tire & Rubber Co.
 Central Research Laboratories
 1200 Firestone Parkway
 Akron, OH 44317

Lieng-Huang Lee
 Senior Scientist
 Xerox Corporation
 Building 114
 Webster, N.Y. 14580

Kenneth Liechti
 Aerospace Engineering and
 Engineering Mechanics Dept.
 College of Engineering
 University of Texas
 Austin, TX 78712-1085

Kenneth E. Luyk
 Technical Specialist
 Product Engineering Division
 Alcoa Technical Center
 Alcoa Center, PA 15069

Shankar Mall
 Department of Engineering Mechanics
 180 Engineering Mechanics Building
 University of Missouri
 Rolla, MO 65401

Lynn Mahoney
 Hysol Division
 Dexter Corporation
 Pittsburg, CA 94565

T. J. Mao
 Head, Polymers Department
 General Motors Research Laboratories
 GM Technical Center
 Warren, MI 48090-9055

George Mayer
 Army Research Office
 P.O. Box 12211
 Research Triangle Park,
 NC 27709

James E. McGrath
 Co-Director
 College of Arts and Sciences
 Department of Chemistry
 Virginia Polytechnic Institute
 and State University
 Blacksburg, VA 24061

Marion F. Mecklenburg
 Department of Civil Engineering
 College of Engineering
 University of Maryland
 College Park, MD 20742

Carolyn E. A. Morris
 P.O.B. 50
 Materials Research Laboratories
 Ascot Vale, Victoria 3032
 AUSTRALIA

Sheldon Mostovoy
 Associate Professor
 Illinois Institute of Technology
 Room 206, Perlstein Hall
 10 W. 33rd St.
 Chicago, IL 60616

James S. Noland, Manager
 Technical Liaison & Contracts
 Engineered Materials Department
 American Cyanamid Co.
 1937 W. Main St.
 P.O. Box 60
 Stamford, CT 06904-0060

Leighton Peebles
 Office of Naval Research
 Code 431
 800 N. Quincy St.
 Arlington, VA 22217

Edwin E. Plueddemann
 Dow Corning Corporation
 P.O. Box 1592
 Midland, MI 48640

Alphonsus V. Pocius
 General Offices 3M
 Bldg. 209-1C-13
 3M Center
 St. Paul, MN 55144

Robert Politi
 Manager, Aerospace Adhesives
 Research
 American Cyanamid Co.
 Bloomingdale Plant
 Havre de Grace, MD 21078

J. N. Reddy
 Engineering Science and
 Mechanics
 Virginia Polytechnic Institute
 and State University
 Blacksburg, VA 24061

Robert R. Reeber
 Army Research Office
 P.O. Box 12211
 Research Triangle Park,
 NC 27709

Robert J. Reynik
 Section Head
 Metallurgy, Polymers and
 Ceramics Section
 Division of Materials Research
 National Science Foundation
 1800 G St., N.W.
 Washington, D.C. 20550

John Romanko
 Senior Engineering Specialist
 General Dynamics
 Mail Zone 5984
 Box 748
 Fort Worth, TX 76101

J. L. Rose
 Department of Mechanical Engineering
 and Mechanics
 32nd & Chestnut Sts.
 Drexel University
 Philadelphia, PA 19104

Daniel Scola
 United Technology Research Center
 MS-24
 Silver Lane
 East Hartford, CT 06108

George Senich
 Polymer Science and
 Standards Division
 National Bureau of Standards
 Washington, D.C. 20234

Louis H. Sharpe
 AT&T Bell Laboratories
 Rm. 1A-316
 Murray Hill, NJ 07974

D. R. Speth
 Bldg. 2040
 Dow Chemical Co.
 Midland, MI 48640

C.S.P. Sung
 Department of Materials Science
 and Engineering
 Room 13-5106
 Massachusetts Institute of Technology
 Cambridge, MA 02139

N. H. Sung
 Tufts University
 Chemical Engineering
 Pearson Laboratory
 Medford, MA 02155

Mark Sylvester
 The Rogers Corp.
 Lurie R&D
 1 Technology Dr.
 Rogers, CT 06263

G. Bruce Taggart
 Senior Staff Member
 Advanced Technology
 The BDM Corporation
 7915 Jones Branch Drive
 McLean, VA 22102-3396

J. Scott Thornton
 President and Technical Director
 Texas Research Institute Inc.
 9063 Bee Caves Rd.
 Austin, TX 78746

Robert Yen-Ying Ting
 Head Materials Section
 Underwater Sound Reference Division
 Naval Research Lab
 P.O. Box 8337
 Orlando, Florida 32856

John D. Venables
 Project Director
 Materials and Chemistry Departments
 Martin Marietta Corporation
 1450 South Rolling Road
 Baltimore, MD 21227

Su-Su Wang
Associate Professor
Department of Theoretical and
Applied Mechanics
216 Talbot Lab
University of Illinois
Urbana, IL 61801

Thomas C. Ward
Adhesion Science Group
405 Davidson Hall
Virginia Polytechnic Institute
and State University
Blacksburg, VA 24061

Steven G. Wax
Program Manager
DARPA/DSO/MSD
1400 Wilson Blvd.
Arlington, VA 22209

Raymond F. Wegman
Materials Engineering
Project Group Leader
DRSMC-SCM-O(D), Bldg. 183
U.S. Army Armament R&D
Center
Dover, New Jersey 07801

Stanley Wentworth
Code DRXMP-OP
Army Materials and Mechanics
Research Center
Watertown, MA 02172

James P. Wightman
Polymer Materials & Interface
Laboratory
Virginia Polytechnic Institute
and State University
Department of Chemistry
Blacksburg, VA 24061

Ben A. Wilcox
Defense Advanced Research
Projects Agency
Department of Defense
1400 Wilson Blvd.
Arlington, VA 22209

Max L. Williams
Dean, School of Engineering
University of Pittsburgh
Pittsburgh, PA 15261

Albert F. Yee
General Electric Co.
Corporate Research and Development
4B20, K-1
Schenectady, N.Y. 12301

APPENDIX III

OVERVIEW OF ADHESION SCIENCE PROGRAM REVIEW/WORKSHOP AT VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY APRIL 30-MAY 2, 1984

A Program Review/Workshop of the Center for Adhesion Science was held at Virginia Polytechnic Institute and State University immediately preceding the NMAB workshop on Reliability of Adhesive Bonds Under Severe Environments. The purpose of a brief review of the former was to bring to the latter, in as concise a form as possible, a summary of the discussions held at VPI that would be germane to the topic of the NMAB workshop.

The workshop was organized so that first-day presentations were by VPI faculty, while the presentations during the next day and one-half were by government scientists or their contractors. The latter speakers were determined by suggestions obtained from the NASA-DOD Committee on Adhesion. The presentations by the five principal investigators at VPI, H. F. Brinson, D. W. Dwight, J. N. Reddy, T. C. Ward, and J. P. Wightman, emphasized the interaction of chemistry, materials, and mechanics while at the same time indicating the nature of their own contributions.

Professor Ward spoke of the type of polymers currently under study to be best suited for high performance under adverse conditions. These adhesives are likely to be "morphologically complex materials" with either two phases or one phase with partial mixing of several components and are also likely to be thermoplastics rather than thermosets. He suggested that a fundamental difficulty with all systems cured under high temperature and pressure is the occurrence of residual stresses. Obviously, methods to quantify the magnitude of residual stresses are needed. Both solid state nuclear magnetic resonance (NMR) and dielectric measurements were shown to provide data of a more molecular nature and to be complimentary to the usual rheovibron information. Inverse gas chromatography was used to provide information about the diffusion of small molecules and/or thermodynamic interactions with cross-linked systems.

Professor Wightman discussed his efforts for the characterization of titanium 6-4, lithium/aluminum, and 7075 aluminum adherends pretreated by

different methods and subsequently bonded with both modified epoxy and polysulfone adhesives. The Ph.D. program of one of his students, J. Filbey, is related to the reproducibility of the surface of pretreated titanium 6-4 adherends. Emphasis is placed on determining the properties of the surface oxide layer, including crystallinity, topography, thickness, surface area/porosity, composition energy, acidity, and environmental stability. In this program Ms. Filbey interacts strongly with faculty and students in mechanical engineering (roughness measurements), mechanics (stress analysis and testing), and materials [fractography using scanning electron or scanning transmission electron microscopy (SEM/STEM), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES)].

Professor Brinson discussed two new methods aimed at measuring the deformation state inside and on the surface of the adhesive layer respectively. The first utilizes embedded strain gauges that have not been used previously, and the second uses moiré interferometry to visualize and measure deformations on the surface of the adhesive layer. The latter work was performed by D. Post under NASA-Langley funding. It was suggested that utilizing both procedures together with a Krieger gauge (American Cyanamid) might produce understanding heretofore not possible.

Professor Brinson also gave experimental results to indicate that viscoelasticity of neat epoxy resins and bonded joints is a significant problem for long-term durability assessments. Apparently, viscoelastic deformations are nonlinear for even small loads and ambient temperatures over a long time scale and are intensified by high temperature, moisture content, and high stress levels. Future analyses for durability predictions must of necessity include these as well as time-dependent cumulative damage and failure concepts.

Professor Brinson and Professor Reddy gave results of finite element analyses of stress distributions in single, thick adherend and crack lap geometries. Results on single lap specimens for shear and peel stresses were shown to be in agreement with a Goland and Reissner solution. Axial stresses were not the same.

E. G. Henneke reviewed various NDT, NDI, and NDE methods currently in use at VPI for composite materials. The same techniques of C-scan, acoustic emission, X-ray radiography, thermography, and neutron radiography are useful for adhesively bonded joints. An important feature outlined was that NDE represents a total systems approach to flaw detection, quality control, flaw tolerance and damage growth, stress analysis, and lifetime prediction and is not limited to merely detecting flaws using a specific technique. Also, bond quality assessment methods are needed.

Surface modification and fractography was discussed by D. W. Dwight as a means to understand why good or bad bonds occur and why they fail. Studies on siloxane-containing block copolymers and their homopolymers were studied using XPS and transmission electron microscopy (TEM). The kinetics and mechanisms of anodized oxide layer growth on titanium 6-4 were found by potentiostatic and galvanostatic techniques. XPS was used to determine the chemical composition and bonding of the oxide and residual contaminants. STEM was used to follow oxide topography development.

Syntheses of polymeric adhesives were discussed by J. E. McGrath, including anionic polymerization, step growth or condensation polymerization, and block and graft copolymerization. He reviewed work to develop styrene, diene, and star-block polymers and their hydrogenated derivatives, poly(arylene ether sulfone imide) copolymers.

On the other hand, G. L. Wilkes reviewed his efforts to use siloxane modifiers for epoxies, including functionally terminated polymethylsiloxane and its statistical copolymers, with methyltrifluoropropyl (TFP) or diphenyl siloxane. Improved fracture toughness was demonstrated, and wear rate was shown to be dramatically reduced.

L. H. Peebles, Jr., addressed the "ilities" of adhesives and indicated that for the Navy these include reliability, processability, durability, and repairability. He suggested that a transdisciplinary approach involving the wide spectrum from chemistry to mechanical engineering is a necessity. As an example, he cited the rubber-to-metal bond in a sonar transducer, which must survive environmental exposures such as seawater, temperature fluctuations, pH, dissolved oxygen, and rapidly varying 200-psi pressures over 10^4 lifetime cycles, among a number of other factors that naturally occur in the life of the transducer. The scientific question posed was, What type of meaningful test (and analysis) schemes can be used to rank various systems during production, in-service damage, and repair with regard to the subject "ilities"? These questions can only be addressed by a broad multidisciplinary approach to the problem of adhesion.

D. Mulville and S. R. Brown spoke of the Naval Air Systems Command's adhesive bonding problems. The former discussed the need for cumulative damage concepts as well as NDT methods for composite bonded structures. The latter reviewed work at the Naval Air Development Center to assess joint durability under adverse environmental conditions using various surface treatments (alkaline peroxide, Pasa Jell, and silanes) on primed titanium adherends bonded with different types of adhesives.

S. E. Wentworth of the Army Materials and Mechanics Research Center gave an overview of U.S. Army programs on adhesion while R. A. Everett, Jr. of the U.S. Army Structures Laboratory, Aviation Systems Command (AVSCOM) discussed failure modes in realistic bonded metal-to-composite joints. Projects such as the all-composite bonded helicopter program (ACAP) and adhesive bonding for lightweight bridging were mentioned. In all cases the potential weight savings were large. The realistic bonded metal-to-composite joint was composed of three large-scale test panels of titanium bonded to graphite/epoxy adherends with a high-strength structural adhesive. Notably, static strengths were 30 percent more than predicted, and failure under both static and fatigue loading was always in the graphite/epoxy adherends and not in the adhesive layer.

E. Becker, J. S. Thornton, and W. L. Hufferd discussed and gave applications of the VISTA (Viscoelastic Stress Analysis of Adhesively Bonded Joints) finite-element code developed with Air Force funding. Professor Becker presented the details of the code (plane strain, nonlinear viscoelastic, time-stepping methodology, small deformation, etc.). Dr. Thornton gave information on using VISTA for the Navy sonar transducer problem, and Dr. Hufferd gave an analysis of crack lap shear geometries.

Sheldon Mostovoy presented a finite element analysis of two adhesive test specimens, the modified-zero-K-gradient (MZKG) specimen and the crack lap-shear specimen. The first is primarily mode III, while the latter is primarily modes I and II. Information on all three modes is often necessary to properly interpret fractures of adhesively bonded structures. For his analysis Dr. Mostovoy used both a SUPERSAP and an ABAQUS finite element code. An assessment of the two was given.

E. J. Ripling discussed a new adhesive scarf joint specimen for mixed mode I-III fracture. Fracture was found to change from center-of-bond to the interface when load changed from monotonically increasing to fatigue.

The NASA-Langley combined analytical and experimental investigation of adhesively bonded composite double cantilever beam and crack lap shear specimens was presented by W. S. Johnson. The specimens were fatigue-loaded, and in all cases failure occurred by debond growth. The total strain energy release rate, G_T , appeared to be the governing parameter, as opposed to either G_I or G_{II} .

Using his previously developed explanation of damage growth in tapered double cantilever beam adhesively bonded specimens, Don Hunston of the National Bureau of Standards gave an explanation of why toughened epoxies are not as effective in increasing composite delamination tolerance as they are in increasing adhesive fracture toughness. The study graphically showed the similarities and differences between the problems of adhesive debonding and composite delamination.

L. H. Lee of Xerox spoke on the new directions for adhesive chemistry. D. K. McNamara of Martin Marietta discussed surface preparation for steel adherends and John Venables of the same organization covered similar topics elsewhere in the proceedings.

Improved hydrothermal stability of adhesive bonds using silane primers was addressed by F. J. Boerio. Reflection-absorption infrared spectroscopy (RAIR) and XPS gave evidence that silane is absorbed into the oxide layer at low pH values to form siloxane polymers. At higher pH levels, 2024 aluminum is etched and alumino-siloxane polymers containing copper ions are formed. The silane and the copolymer can form interpenetrating networks during lamination of the copolymer onto the primed substrate.

T. L. St. Clair of NASA-Langley emphasized the need for high-temperature structural adhesives for aerospace applications. One area focused on was the development of an adhesive that could be useful for supersonic aircraft where skin temperatures may reach 177°C (350°F) and the lifetime should exceed 50,000 hours. He described a LARC-developed thermoplastic polyimide and a siloxane-containing polyimide. Durability studies of the former were conducted for over 20,000 hours at 232°C (450°F) with thermoplastic polyimide bonded titanium 6-4 adherends, using both Passa Jell and "Boeing anodizing" surface treatments.

APPENDIX IV

BIOGRAPHICAL SKETCHES OF THE COMMITTEE

HALBERT F. BRINSON has a variety of degrees from several institutions: BCE and MS in Civil Engineering from North Carolina State University; PhD in Engineering Mechanics from Stanford University and postgraduate study in Theoretical and Applied Mechanics at Northwestern University. This diverse background is utilized in his present position as Chairman of the Center for Adhesion Science at Virginia Polytechnic Institute and State University. He served the Army as research officer and worked in industry at Lockheed Aircraft Co. as a stress analyst. He served from 1978 to 1979 as president of the Society for Experimental Stress Analysis.

K. LAWRENCE DEVRIES, a native of Utah, is Chairman of the Department of Mechanical Engineering at the University of Utah from which he received his BS and PhD degrees. He has worked at Convair Aircraft Co. and served a tour at the National Science Foundation. He has specialized in stress analysis, mechanical behavior of materials, and molecular phenomena associated with deformation.

ALAN N. GENT was born in England, receiving his education at London University, where he obtained a PhD in physics in 1955. He is Professor of Polymer Physics and Dean of Graduate Studies and Research at the University of Akron. Dr. Gent is the recipient of many awards, including the Bingham Medal (Society of Rheology) and the Colwyn Medal (Plastics and Rubber Institute). In 1978 he was president of the Adhesion Society.

SERGE GRATCH heads the Material and Chemical Sciences Laboratory of the Ford Motor Co. and is the recent past president of the American Society of Mechanical Engineers. Educated at the University of Pennsylvania, he has taught at both the University of Pennsylvania and at Northwestern University. From 1951 to 1959 he was a Senior Research Scientist at Rohm and Haas Co. Since 1961 he has held various positions at Ford. His interests have ranged from thermodynamic properties of gases to materials and processes for automobiles.

LIENG-HUANG LEE, a native of China, received his MSC and PhD degrees in chemistry from Case Institute of Technology. He has both practiced chemistry and taught in China. In 1958 he joined the Dow Chemical Co. and in 1968 moved to the Xerox Corporation, where he is now a senior scientist. His research interests are in polymer friction and wear, adhesion, and surface chemistry.

JAMES S. NOLAND has bachelor degrees in both chemistry and education; his MS and PhD degrees are from the University of Iowa. He has held a number of positions with the American Cyanamid Co. His research interests are in new resin systems.

JOHN D. VENABLES worked as a physicist at the Parma Research Center of Union Carbide before his move to Martin Marietta Laboratories. His BS degree is from Case Institute of Technology; PhD from the University of Warwick. Dr. Venables interests have included defect structure, radiation affects of solids, and high-temperature ceramics as well as adhesives.