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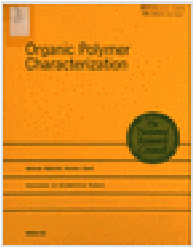

Organic Polymer Characterization: Report (1977)

Pages
159

Size
8.5 x 10

ISBN
030934154X

Committee on Organic Polymer Characterization; National Materials Advisory Board; Commission on Sociotechnical Systems; National Research Council

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NMAB-332	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Organic Polymer Characterization		5. TYPE OF REPORT & PERIOD COVERED Final Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) NMAB Committee on Organic Polymer Characterization		8. CONTRACT OR GRANT NUMBER(s) MDA 903-74-C-0167
9. PERFORMING ORGANIZATION NAME AND ADDRESS National Materials Advisory Board National Academy of Sciences Washington, D. C., 20418		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Department of Defense - ODDR&E Washington, D. C., 20301		12. REPORT DATE 1977
		13. NUMBER OF PAGES 155
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

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

Organic Polymer Characterization
Materials Character
Properties of Materials
Structure-Property Relations in Polymers
Structural Design Considerations
Characterization Techniques
Fracture
Problems in Methodology of Testing
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report attempts to define those properties of organic polymers that are critical to their use in current and advanced structural applications. It discusses and evaluates the characterization methodology that is available to measure and control those properties. It suggests some specific areas in which this technology can be employed to achieve improved performance and reliability through its application to procurement and quality control procedures. Case studies are

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ORGANIC POLYMER CHARACTERIZATION

Report of

The Committee on Organic Polymer
Characterization

NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
National Research Council

Publication NMAB-332
National Academy of Sciences
Washington, D. C.
1977

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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 competences and with regard for appropriate balance.

This 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.

This study by the National Materials Advisory Board was conducted under Contract No. MDA-903-74-C-0167 with the Department of Defense.

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This report attempts to define those properties of organic polymers that are critical to their use in current and advanced structural applications. It discusses and evaluates the characterization methodology that is available to measure and control those properties. It suggests some specific areas in which this technology can be employed to achieve improved performance and reliability through its application to procurement and quality control procedures. Case studies are presented to illustrate the utilization of characterization. Conclusions and recommendations are presented. A list of more than a hundred useful methods of characterization with Committee commentary on use and limitations is given in an appendix.

ACKNOWLEDGMENTS

The Committee would like to acknowledge the contributions of the following individuals and organizations: Raymond F. Boyer, Midland Macromolecular Institute; R. B. Gosnell, WRD Whittaker Corporation; Frank N. Kelley, U. S. Air Force Materials Laboratory; Paul Legally, U. S. Navy, Ships Research and Development Center; Paul Lindenmeyer, Boeing Aerospace Company; Clayton May, Lockheed Missile and Space, Inc.; H. Meisselman, Defense Materiel Standards and Specifications Office; Lowell E. Netherton, BASF Wyandotte Corporation; T. S. Noland, American Cyanamid Company; Harvey Parry, Hysol-Dexter Company, Edward D. Sayer, General Electric Company; Morris A. Steinberg, Lockheed Aircraft Corporation; Max L. Williams, University of Pittsburgh; Robert Wittman, U. S. Air Force, Flight Dynamics Laboratory; Donald Yurek, 3M Company; Giuliana C. Tesoro, Massachusetts Institute of Technology; C. M. Guttman, National Bureau of Standards.

Special thanks are due to the American Chemical Society and the American Physical Society for response to the request for information on characterization methods.

The staff support of Dr. Robert S. Shane in the preparation of this report is gratefully acknowledged.

Charles G. Overberger
Chairman

PREFACE

The National Materials Advisory Board of the Commission on Sociotechnical Systems, National Research Council, was asked by the Department of Defense Office of Research and Engineering and the National Aeronautics and Space Administration to "initiate a study to update the previous 1967 MAB study on the characterization of polymeric and organic materials."

The Committee was established 22 April 1974.

Details of the initiation, scoping, and organization of the work of the Committee are given in Chapter 1. A feature of the Committee's work is the use of outside information sources through invited tutorial lectures and questionnaires.

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ORGANIC POLYMER CHARACTERIZATION

CONTENTS

CHAPTER 1

HOW TO USE THIS REPORT
(INTRODUCTION, METHODOLOGY, CAVEATS)

The existing basic National Materials Advisory Board program provides advisory services in materials research and development in response to requests of the Department of Defense and the National Aeronautics and Space Administration. A task was assigned to conduct a study to update Chapter 6 of the 1967 Materials Advisory Board study of the Characterization of Materials.* This chapter addressed polymeric and organic materials.

The specific charge was as follows: "Initiate a study to update the previous 1967 MAB study of the characterization of polymeric and organic materials* in order to define critical behavioral parameters and characterization methods, techniques and procedures, as a feasible basis for evolving adequate, functional materials specifications and quality control procedures, for certain types of materials of special interest. Since the class of materials to be covered here is large, a first step in the study perforce will be the determination of a very limited number of specific materials of primary current and future importance to the Department of Defense/National Aeronautics and Space Administration. With this determination the study will concentrate on ways to best describe the materials in terms of atomic structural and compositional character, as well as their behavioral or performance properties, in order to help insure that such materials can be made and reproduced uniformly and reliably. Because of the complexity, significance and long-time neglect of this subject, it may be necessary to conduct the total study in progressive phases."

To interpret the needs of the Department of Defense and the National Aeronautics and Space Administration, an advisory group was convened on 7 February 1976 with representatives of the Office of Defense Research and Engineering, the National Aeronautics and Space Administration, the Army, the Navy, the Air Force, the Advanced Research Projects Agency, the Defense Materiel Specifications and Standards Board, technical experts from academia and industry, and NMAB members and staff. From the work of this group came certain broad outlines which were to guide the study Committee in its work.

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*MAB-229-M Characterization of Materials, Washington, D. C., 1967.

It was recognized that the study should address several audiences. These were identified as resource allocators, polymer scientists, those who design with polymers, those who produce products containing polymers, and end-users of products containing polymers.

Acknowledging the validity of the last statement of the Charge, the Committee was advised to defer to another phase (and another Committee) the characterization problems of composites, but as will be evident, the problem of characterizing the polymers used in composites could not be divorced from the general problem of characterizing polymers since polymers are often used in combination with other materials in engineering applications.

Further, the Committee was advised to direct its attention primarily to engineering (high-performance) polymers, e.g., epoxy resins, polyimides, polyheterocyclics, etc. It was suggested that the technical aspects of the work should address: (a) the chemical and solid state structure of polymers; (b) parametric values (mechanical, electrical, thermal--but emphasizing mechanical) in various environments, temperatures, pressures, solvent exposure, etc., particularly in light of molecular structure and processing history of the polymer; (c) properties of importance to end-users, e.g., wear rate, erosion rate, etc. And particularly, the Committee was advised to look at the interfaces of those areas including the application of the tools of polymer characterization from a societal point of view.

Chapter 6 of the MAB Report 229-M was considered to be still valid with regard to area (a) above; the other areas would require more intensive study. Of particular concern to the Advisory Group was the limited distribution of MAB 229-M; it was considered essential for the new report to have much wider distribution, particularly in academia.

Accordingly, in May of 1974 the National Materials Advisory Board Committee on Organic Polymer Characterization was constituted. The general modus operandi of the Committee was to identify and assess the state of the art, identify missing areas of knowledge, identify and assess current relevant work in progress, draw conclusions, make implementable recommendations, and estimate the benefits which might be expected if recommended courses of action were pursued. Specifically, the Committee identified its scope, the outline of its study, and its particular intent to use case studies as a method of exemplifying its study, conclusions and recommendations. The discussion in Chapter 3, "Statement of the Problem", states the charge adopted by the Committee, defines characterization as understood by the Committee, and details succeeding chapters which embody this study. Chapter 4 endeavors to give a summary of current information on the known relationships between physical and mechanical properties of polymeric materials and their chemical constitution and morphology. Chapter 5 reviews the critical needs of designers in order to exploit the special properties of polymeric materials to their utmost potential. Chapter 6 discusses polymer characterization in overall terms and presents an approach to the general problem. In addition, new characterization techniques are described which are germane to the case studies in this report. Chapter 7 points out and exemplifies through three case studies the relationship between characterization techniques and their utilization. The chapter opens with an analysis of the case study method.

For the reader who wants only the conclusions and recommendations of this Committee, Chapter 2 summarizes the findings of the Committee's studies and deliberations.

A caveat should be noted: the Committee's attention was focused on engineering (high-performance) polymers. A second caveat lies in the limitations of the data used. It was not possible to identify the effects of small changes in the environment, trace elements and compounds on the reported properties of polymers. A third caveat lies in the commercial confidentiality and proprietary nature claimed to exist in some of the cases studied.

Not all of the information furnished to the Committee will be found in this report since a substantial amount was furnished for background and not for citation or attribution. This is particularly true in the case study on adhesives.

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CHAPTER 2

CONCLUSIONS AND RECOMMENDATIONS

Chapter 3*

Conclusion: Optimum effectiveness in the utilization of organic polymer materials in advanced applications is highly dependent on the establishment of confidence in their reliability and reproducibility.

Recommendation: Learn to predict long-term performance from an accumulated data bank of information on well-characterized materials.

Recommendation: Develop meaningful structure/property/performance relationships for polymeric materials. Include them in a referenced data bank.

Recommendation: Strive for improved communication and mutual understanding of the problems faced by polymer scientists, design and materials engineers, manufacturers, fabricators, and users in the development and utilization of organic polymeric materials.

Chapter 5*

Conclusion: A close analysis of the total materials requirement of a system, subsystem, component, or part should be a prerequisite to establishing the total design requirements.

Recommendation: Make materials choices for design based on a logical process outlined in this chapter.

Conclusion: Irrespective of the design analysis technique employed to select materials, part testing should be performed. This is a necessary (but not sufficient) element of material selection and qualification.

Recommendation: Perform simulated tests under controlled conditions to evaluate the performance of the part when used in a manner similar to that for which it is intended under conditions subject to measurement and recording, and with enough replication and variety to make statistical analysis of the results valid.

Chapter 6*

Conclusions: Although many techniques for characterizing polymers are now available, a large fraction are limited in application to ideally simple systems. On the other hand, most polymer systems to be characterized are formidably complex.

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*Chapter from which the conclusion(s) and recommendation(s) were taken.

Many so-called characterization tests are of the "specification use" type, in which a specification is set with the hope that it will insure a certain end-use performance, but often, in fact, it does not.

There is too little basic understanding of the relations between polymer structure and end-use performance.

Many of the manufacturers of equipment for polymer characterization know little about the manner in which their equipment is used, over and above its application to standard tests.

The fact that there has been little advance in our knowledge and application of polymer characterization over the last ten years is related to the unusual complexity and large number and variety of polymers as compared to other materials.

The best solution to the problem of adequate characterization of polymers is a compromise between complete detailed knowledge of structure (unattainable) and total reliance on a battery of end-use tests (inadequate).

Lamentably, polymer characterization methods of fundamental significance are being used less and less as time goes on.

More practice of basic characterization techniques in industry is needed. Better instrumentation is required for many polymer characterization methods.

More personnel skilled in polymer characterization are required. Granting agencies should be encouraged to supply funds for their academic training, and industry should be encouraged to hire and use them.

Recommendations: Skills must be developed to characterize complex, rather than just simple, polymer systems, probably through application of judicious combinations of techniques. Incentive should be provided to academic efforts in this direction by appropriate granting agencies.

Research is needed to elucidate the relations between polymer structure and end-use performance. Cooperative academic-industry and academic-governmental research, with appropriate support, is recommended.

Manufacturers of equipment for polymer characterization should work more closely with users to develop better understanding of how their equipment is used and thus be more responsive to users needs.

Programs are required to educate users of characterization techniques on what they can and cannot do, especially in application to complex polymer systems. Continuing education techniques are suggested.

Government subsidy of instrumentation development costs should be considered, where necessary, by granting agencies.

CHAPTER 3

STATEMENT OF THE PROBLEM

This ad hoc Committee of the National Materials Advisory Board was convened to address the question of how, or whether, modern analytical technology can contribute to the better characterization of organic polymeric materials in order to permit their more efficient utilization by the Department of Defense and other Federal Government agencies. The areas of particular concern are those in which polymeric materials are stressed near their ultimate limits, i.e., regions where small variances or deficiencies in properties might override built-in safety factors and result in catastrophic in-service failures of critical components. It was early recognized that the resolution of these questions could involve a significant change in procurement philosophy and, particularly, that it could logically lead to the Department of Defense utilization of compositional specifications in lieu of, or superimposed on, performance specifications.

The Committee on Organic Polymer Characterization, consequently, has taken as its charge the following activities which are of interest to the government as well as the scientific and technical communities: (1) to attempt to define those properties of polymeric materials that are critical to their proper use in current and advanced structural applications; (2) to discuss and evaluate the characterization methodology that is available to measure and control those properties; (3) to suggest some specific areas in which this technology can lead to improved performance and reliability through its application to procurement and quality control procedures.

It is difficult to state which specific properties of a polymeric material are critical, since this will depend ultimately on its end use. However, if we can fully define the end-use conditions and requirements, we should be able to specify in general terms some principal attributes that the polymeric material must have. These are the parameters that the design engineer requires--physical and mechanical properties and, in particular, how these vary with time under service or operational conditions (humidity, temperature, stress, etc.). These are often the sum of semi-independent and often opposed characteristics and normally are not the basic molecular parameters determined in the initial characterization of a new polymeric material. That is not to say that there is no relationship between the ultimate physical properties of a polymer and its molecular constitution; indeed some such relationships are known and are useful; they do not necessarily provide a direct guide to the properties of a final derived product.

An early report of the National Academy of Sciences/National Academy of Engineering, Characterization of Materials, (MAB 229-M) did discuss polymeric materials but addressed itself primarily to molecular characterization parameters and the morphology of polymers. Clearly then, if the present Committee is to address the larger problem and is to provide information useful to designers and users, another approach must be sought.

The Committee therefore defines characterization in a very broad sense--Characterization should describe those features of the chemical composition and molecular structure of a material that make it suitable for a particular end-use and that are necessary and sufficient for precise replication of the material. To achieve this evaluation, appropriate methods of characterization need to be identified and defined as specifically as possible: (a) to insure satisfaction of design requirements; (b) to assure reliability of in-service performance; and (c) to provide guidance as to allowable limits of variation of critical molecular or physical parameters. This report provides guidance to users to aid them in writing realistic specifications to assure that they obtain suitable and reproducible products; to manufacturers so that they can institute reasonable, cost-effective quality control procedures; and to engineers and scientists so that they can develop the data base of material properties needed by designers.

The military services, as well as the civilian sector, have been increasingly attracted to the use of polymers as engineering materials because of their frequent cost, weight and performance advantages, and their applicability in those areas where design and properties are more important than composition of material. However, the average designer is not yet sufficiently familiar with the subtle differences in behavior of polymers and metals under similar stresses; this can lead to improper design with the newer materials. It is hoped that this document will inspire technological advances that will help dispel some of the mysticism associated with the design and fabrication of polymer-containing products and give a metals-oriented designer the confidence he needs to prescribe polymeric materials for severe service applications.

Succeeding chapters in this report will deal more specifically with the methodology by which the stated objectives are to be attained. These chapters are summarized in Chapter 1, Introduction, Methodology, Caveats.

In summary, this report attempts to give a realistic appraisal of the state-of-the-art in polymer characterization as it can be applied to current and future materials development and procurement programs. It also provides useful guidance to government and industry on the research and development characterization programs required for the development and implementation of an improved characterization technology. The recommendations should lead, in the short-term, to a marked increase in reproducibility and reliability of polymer performance; in the mid-term, to the increasing specification of polymeric materials for critical applications and to the identification of equivalent alternative or substitute materials. The predictability of long-term performance from an accumulated data bank of information on well-characterized materials, and the development of meaningful structure/property/performance relationships will continue to be a long term goal of polymer characterization.

Optimum effectiveness in the utilization of organic polymeric materials in *advanced* applications is highly dependent on the establishment of a feeling of confidence in their reliability and reproducibility. This confidence can be developed, in part, by better communication among polymer scientists, design and materials engineers, manufacturers, fabricators and users, and by the growth of a mutual understanding of the problems others face in the development and utilization of organic polymeric materials.

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CHAPTER 4

STRUCTURE-PROPERTY RELATIONS IN POLYMERS

INTRODUCTION

The common central structural feature of organic macromolecules is the chain of covalently bonded atoms. Bond lengths and bond angles are rather rigidly fixed, but restricted rotation about single bonds permits a polymer chain to assume a wide range of three-dimensional conformations. At elevated temperatures, bond rotation is frequent; the polymer chain changes rapidly from one conformation to another. This micro-Brownian motion confers flexibility upon a macroscopic specimen. At low temperatures, the chains are immobilized, and the specimen hardened, by either of two mechanisms: crystallization (packing into a crystal lattice) or vitrification (forming a glassy amorphous solid). The crystalline melting point T_m, and the glass transition temperature, T_g, are important characteristics of a given polymer.

The molecular structure of a particular polymer has two aspects, "chemical composition" and "molecular architecture". The term "chemical composition" refers to the local molecular structure--the nature of the units that make up the chains (including the stereochemical structure of these units). "Molecular architecture" refers to molecular structure in the large: average molecular weight, molecular weight distribution, branching, crosslinking, etc. In the case of network polymers it refers to the average molecular weight between crosslinks, the number and lengths of dangling tails, and many subtle aspects of network topology.

In approaching the problem of structure-property relationships, the first and simplest step is to examine the relationships between molecular structure and the values of T_m, and T_g. Having done this, one is faced with the difficult task of characterizing the quantitative mechanical behaviors of polymers (and relating them to structure) in each of various regimes: high temperature viscoelastic fluids; glassy amorphous solids; semi-crystalline solids containing flexible amorphous regions (between T_g and T_m); semi-crystalline solids containing glassy amorphous regions; highly crystalline solids; metastable, supercooled amorphous polymers; rubbery elastic networks; etc. In some of these regimes "structure" refers simply to molecular structure; in others (notably glassy and crystalline states), properties depend not only on molecular structure but also on supramolecular structure--molecular orientation, crystalline morphology, etc.

DEPENDENCE OF T_m AND T_g ON MOLECULAR STRUCTURE

The crystalline melting point (T_m) and glass transition temperature (T_g) of a polymer provide a rough characterization of the polymer properties; they also provide reference points for the various regimes within which the quantitative evaluation of properties must be made. How do T_m and T_g depend on molecular structure?

In addressing this question, attention will be initially confined to a single molecular architecture--high molecular weight linear chains. Such chains will be arbitrarily classified into five broad structural classes: I - perfectly repeating "matched pearl necklace"; II - random copolymers; III - D-L and cis-trans "copolymers"; IV - block copolymers; V - short-unit chains which assume helical conformations.

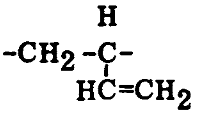
Class I chains, because of their structural regularity, usually pack efficiently into a crystalline lattice. They generally exhibit well-defined values of T_m and T_g. (However, the prototype linear polyethylene, crystallizes so rapidly that it cannot easily be trapped in the glassy amorphous state; consequently, the values of its T_g has been a matter of controversy.)

The crystalline melting point of linear polyethylene is approximately 140°C. If methylene groups of polyethylene are replaced regularly by other moities in the chain backbone higher or lower values of T_m are observed. Two factors govern the magnitude of T_m: chain flexibility and inter-chain forces. Flexible units (such as ether, ester, or sulfide) result in lowered melting points. Rigid units (such as p-phenylene) result in higher melting points. Strong intermolecular forces (such as hydrogen bonds) yield high melting points[1].

Within Class I, the same structural features which promote high crystalline melting points also yield high values of T_g. Consequently, there exists a rough correlation between T_m and T_g for this class of polymers[2]. By controlling chain stiffness and intermolecular forces, polymers with high values of T_m and T_g or low values of T_m and T_g can readily be designed; but it is not possible to control independently these two characteristic temperatures.

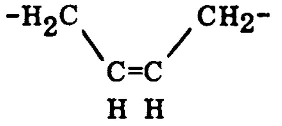
Class II polymers--random copolymers--fit less neatly into crystal lattices. Melting points are depressed and the degree of crystallization is reduced. (A few special exceptions exist, in which the two monomer units are sufficiently matched in geometry that they can interchangeably occupy sites in a common lattice.) Since Vitrification does not involve fitting into a crystal lattice, the glass temperatures of copolymers are not depressed by the chain irregularity. Consequently, random copolymers do not follow the T_m-T_g correlation characteristic of Class I polymers[3].

Class III is primarily made up of vinyl and diene addition polymers. When a vinyl monomer, $CH_2 = CHX$, is subjected to additional polymerization a stereochemical problem is encountered at every second carbon atom of the chain. The substituent X can extend above or below the plane of the extended zigzag chain, corresponding to a D- or L- configuration of the chain carbon atom in question[4]. When the addition polymerization is carried out with a "stereo-specific" catalyst, the polymer may be a regular structure: "isotactic"(repeating DDDDDD, etc.), or "syndiotactic" (perfectly alternating DLDLDLD, etc.)[5]. On the other hand, free radical addition polymerization tends to produce a rather random ("atactic") copolymer of the D- and L- configuration: DDLDLLDLDDLDLLD, etc. Consequently vinyl polymers produced by free radical polymerization tend to be permanently amorphous or at most to exhibit only a small amount of crystallinity. In the case of dienes a single pure monomer can enter the polymer chain in several different manners. The simplest example is butadiene, $CH_2=CH-CH=CH_2$, which upon polymerization can convert to a 1, 2-chain unit (with a pendant vinyl group which can assume atactic, isotatic and syndiotactic configuration), or to a cis-1, 4- or trans-1, 4- chain unit:

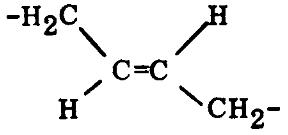


$-CH_2-\underset{HC=CH_2}{\overset{H}{C}}-$

1,2 unit

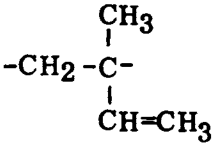


cis-1, 4 unit



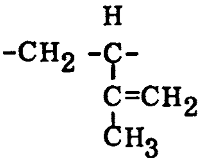
trans-1, 4 unit

Polybutadiene formed by high temperature, free-radical addition polymerization is a copolymer of these three kinds of structural units. With isoprene, (2-methyl butadiene, the number of ways the unit can enter the polymer chain is still larger; for example, the 1, 2- unit with a pendant vinyl group is structurally different from the 3, 4- unit with a pendant isopropenyl group:



$-CH_2-\underset{CH=CH_3}{\overset{CH_3}{C}}-$

1,2 unit



$-CH_2-\underset{\underset{CH_3}{C=CH_2}}{\overset{H}{C}}-$

3,4- unit

Synthetic polisoprene, prepared by free radical polymerization of isoprene monomer, is a copolymer of six structurally distinct kinds of isoprene chain units. Unlike natural rubber, which is a regularly repeating Class I structure (cis-1, 4) such synthetic polyisoprene does not crystallize. On the other hand, by the use of the appropriate stereospecific catalyst, isoprene monomer can be converted to a regular Class I polymer with the same structure as natural rubber[6].

Block copolymers (Class IV) are made up of two (or more) different monomer units, arranged in long blocks of each type of unit. For example, a chain consisting of a block of 500 A units followed by a block of 500 B units and another block of 500 A units is an ABA triblock copolymer. If an A-block corresponds to a Class I chain structure, it can crystallize in the normal poly-A crystal lattice, and can exhibit a value of T_m which is only slightly depressed compared to that of the poly-A homopolymer. Even if the individual blocks are non-crystallizing atactic addition polymers, they are ordinarily mutually immiscible (if long), and undergo a micro-segregation into separate microphases, or "domains". These domains may develop into regular geometrical arrays, the for of which depends upon the relative volume fractions of the individual blocks. If the volume fractions are approximately equal, a laminar domain morphology emerges, with laminar thickness depending upon block lengths. If B-blocks constitute the major part of the copolymer, the B-phase tends to be continuous, with cylindrical or spherical A-domains dispersed within it in a regular fashion. The properties of such a block copolymer depend upon the composition and length of each block, and the domain morphology assumed by the chains. Because of micro-segregation, the individual components exhibit their own characteristic T_m and T_g values (slightly modified). Thus, a segregated block copolymer will normally exhibit two distinct glass transitions, in contrast to the single intermediate glass transition commonly seen in random copolymers[7].

Whereas polyethylene, polyamides, and polyesters assume an extended planar zigzag conformation in the crystal lattice, many short* unit polymers twist into some helical conformation (Class V). In isotactic polyolefins, the extended planar conformation is sterically forbidden; by twisting into a regular helix, the chain relieves the steric strain. If the angular twist of each unit (relative to its predecessor) is a rationale fraction of one revolution, then the spatial orientation of the alkyl groups will exhibit a definite repeat distance. If the individual twist angle is $2\pi/n$, successive alkyl groups will be oriented at the angles $2\pi/n$, $4\pi/n$, $6\pi/n$, etc., and the orientation will repeat with a periodicity of n groups. If the individual twist angle is $4\pi/n$ with n odd, the chain will go through two helical turns before repeating. More generally, if the twist angle per group (measured in revolutions) is given by the irreducible fraction m/n, then the substituent group orientation will repeat after n units, with m complete turns appearing in the repeat sequence. The helical conformation is effectively a rod, and packs parallel to neighboring rods in the crystal lattice[8].

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*"Short" is used here to mean a chemically repeating block of 2 or 3 backbone atoms.

While the effects of chemical composition upon the crystallization and vitrification processes have been emphasized, molecular architecture also influences these processes. Branching and crosslinking introduce points of irregularity which cannot easily fit into a crystal lattice. This can reduce the degree of crystallinity, the value of T_m and the rate of crystallization. Thus, branched polyethylene is considerably less crystalline than linear polyethylene, and consequently softer and less dense. Vulcanized natural rubber crystallizes much more slowly than unvulcanized; and a high degree of vulcanization can completely prevent crystallization[9]. Introduction of crosslinks into a glassy amorphous polymer increases the value of T_g [10].

Brief comments regarding several specific polymer species are presented to illustrate the above general principles regarding qualitative polymer structure-property relationships.

POLYETHYLENE

Polyethylene falls into the "matched pearl" structure category. It consists of a chain of methylene ($-CH_2-$) groups. It is probably the most elementary of all polymers and even it shows wide variations in properties. The property variations are for the most part a consequence of slight imperfections in the chains. An occasional branch in the chain can interfere with packing and introduce a tertiary hydrogen which is prone to oxidative attack. Slight branching leads to lower density, lower moduli and higher solubility under milder conditions, and perhaps a predisposition to crosslinking. More perfect chains of methylene groups prepared from methylene radicals or by way of low pressure Ziegler-Natta catalysis tend to be more dense, have higher moduli and are more brittle. In either case, the small hydrogen substituents exercise very little restiction on the mobility of the carbon-carbon backbone chains.

POLYPROPYLENE

If every other carbon in a polyethylene chain has a hydrogen substituent replaced by a methyl group, the resulting polymer is polypropylene. If the arrangement is completely random, the polymer lacks crystallinity and is readily soluble. If the methylene substituents occur in stereoregular fashion on every other carbon, the polymer can crystallize.

The side chain (dangling) methyl groups tend to prevent extremely efficient packing of the polypropylene molecular chains so the resulting polymer density is a little lower than that of polyethylene. There is a chain stiffening effect which shows up in slightly higher moduli (flex, tensile, etc.).

Polypropylene differs chemically from polyethylene in resistance to oxidation. In polypropylene every other backbone carbon is attached to three other carbon entities, and one hydrogen atom that is more suceptible to oxidation (degradation) than the other hydrogen atoms. Consequently, although polypropylene can maintain general physical properties at temperatures higher than polyethylene (because of its higher melting point, T_m), it must be protected by antioxidants or it will fail quicker than polyethylene in use. Another useful and practical consequence of the slight oxidative instability is that a little surface oxidation promotes ready adhesion and causes the material to retain coatings more satisfactorily.

POLYSTYRENE

Commercial polystyrene is atactic, and therefore non-crystalline. (Isotactic polystyrene can be synthesized but is not commercially produced.)

Polystyrene is a transparent, brittle, glassy polymer that withstands deformation under load up to about 90°C. It is relatively soluble in a wide variety of solvents at room temperature because it is not crystalline. It has excellent electrical properties and poor to fair mechanical properties. Utility would be severely limited if it were not possible to modify or design around its brittle character. The key to wide use of polystyrene was the discovery that if the right kind and right amount of rubber of the right particle size could be dispersed in it, then the composite became relatively tough. The rubber particles tend to interrupt cracks and prevent their propagation across the molded parts. Later developments included a grafting of styrene onto rubber to effectively build in the toughening agent.

POLY(VINYL CHLORIDE) (PVC)

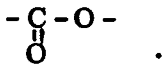
Poly(vinyl chloride) is a high melting (softening) glassy material which has excellent resistance to burning. Its density is about 1.4. It is soluble at room temperature in several solvents. PVC is glassy for the same reason as is polystyrene. It may be toughened by blending with a specific rubbery polymer (chlorinated polyethylene) or by plasticizing with high boiling liquids.

POLYACRYLONITRILE

Polyacrylonitrile is essentially a polyethylene backbone with highly polar nitrile (-CN) groups dangling on every other carbon (average). It has an atactic structure, but it has a very high softening point due to intermolecular attraction. It is soluble only in some polar solvents.

ALIPHATIC POLYESTERS

Polyesters derived from long chain diols and diacids have high ratios of methylene to ester units:



$$-\underset{\underset{\displaystyle O}{\|}}{C}-O- \quad .$$

The methylene units tend to dominate the property profile yielding polyethylene-like properties. With shorter chain diols and diacids, the concentration of ester groups is greater with increased polarity. The effect of the polarity of the carbonyl units and increased flexibility of the carbon-oxygen-carbon bonds becomes apparent. Melting or softening ranges are lowered, adhesion to polar surfaces increases, and the products are soluble in a variety of oxygenated solvents. As a class, aliphatic polyesters have found very little use in structural applications because of their low softening temperatures.

AROMATIC POLYESTERS

Substitution of symmetrical aromatic dibasic acids for aliphatic acids increases both the glass transition and crystal melting points. The product from ethylene glycol and terephthalic acid provides the basis for polyester textiles and oriented polyester film. The increased chain rigidity provided by the p-phenylene unit in the chain is responsible for the higher melting point and glass temperature of this polymer.

ALIPHATIC POLYAMIDES

The polar amide grouping:

$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{\|}}{N}-$$

provides strong electron donating and accepting capability. This promotes extensive intermolecular hydrogen bonding and is a partial explanation of why these polymers tend to crystallize readily, are soluble in highly polar solvents, and have higher melting points than aliphatic polyesters. As in the case of polyesters, long chain diamines and diacids combine to yield methylene-rich polymers which become more like polyethylene as the methylene ratio increases.

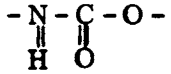
AROMATIC POLYAMIDES

Linear polyamides containing phenylene units in the chain, such as poly(ethylene terephthalamide), exhibit both chain rigidity and strong hydrogen bonding, and consequently have extremely high melting points.

Completely aromatic polyamides (aramids) have higher melting points and lower solubilities than poly(ethylene terephthalamide).

LINEAR POLYURETHANES

Polyurethanes incorporate linkages of both polyamides and polyesters:



$$-\underset{\substack{\| \\ H}}{N}-\underset{\substack{\| \\ O}}{C}-O-$$

and, as predicted, exhibit properties somewhat in between. Sulfur-containing analogs of the oxygen compounds are known and their properties are predictable.

PHENOL-FORMALDEHYDE RESINS

In the area of thermosetting polymers, phenol-formaldehyde resins were the first ones to be synthesized; they still represent a very large percentage of utilized polymers. Phenol can react with formaldehyde in the presence of acid or base to introduce methylol ($-CH_2OH$) groups at the positions ortho or para to the phenolic hydroxyl group. The methylol groups can in turn react with more phenol to form methylene bridges with concurrent elimination of water molecules. In practice, the reaction is advanced to a stage short of total crosslinkage and insolubilization and stopped (cool-catalyst neutralization). The pre-polymer is then mixed with fillers, additional catalyst, and modifying agents to produce molding compounds. Fillers may be eliminated for adhesive or coating usage.

Catalyzed phenolic pre-polymer ("B"-stage) is heated to effect final cure to the "C" stage. Additional methylene bridges are formed with the elimination of water. The end product is very thermally stable, somewhat hydrophilic due to residual phenolic groups, has excellent solvent resistance, is usually black and tends to be on the brittle side, as are most polymers which are highly crosslinked.

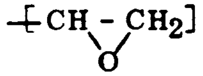
UNSATURATED POLYESTERS

This group was the next major family of thermoset polymers which were developed. For all practical purposes they are relatively low molecular weight polyesters derived from di- and trifunctional acids and polyols with the added feature of unsaturation. The prepolymers are formed by a typical polyester condensation route; conversion to an infinite network proceeds by way of a radical-induced vinyl polymerization. The principal source of unsaturation is derived from maleic or fumaric acid precursors. The unsaturated prepolymers (similar to prepolymer phenolics) are frequently blended with styrene or other unsaturated monomers, compounded with fillers and catalyzed with peroxides. Curing can occur at room temperature but it is frequently accelerated by heating.

The products are insoluble and infusible, relatively colorless, chemically resistant, relatively thermally stable and brittle. Flexibility may be modified slightly by design of the basic molecule or through the use of reactive plasticizers, but one must usually trade dimensional stability or some other property for a gain in flexibility. Polyesters, unlike phenolic resins, do not split off small molecules (water) during cure so they may be processed in thick sections without requiring pressure.

EPOXY RESINS

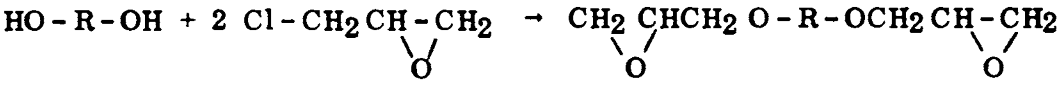
Epoxy resins represent the last major class of thermoset polymers that we will consider in this section of the report. Their key feature is the 1, 2-epoxide group:



$$-\!\!\left[\underbrace{CH-CH_2}_{O}\right]$$

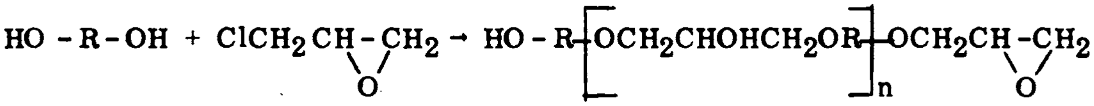
that can react with acids, anhydrides, amines, or reactive hydrogen in general to produce new chemical bonds. The most common epoxy resin building block is the reaction product of bisphenol-A and epichlorohydrin.

I.



$$HO-R-OH + 2\;Cl-CH_2\underbrace{CH-CH_2}_{O} \rightarrow \underbrace{CH_2\;CH}_{O}CH_2\;O-R-OCH_2\underbrace{CH-CH_2}_{O}$$

II.



$$HO-R-OH + ClCH_2\underbrace{CH-CH_2}_{O} \rightarrow HO-R\left[OCH_2CHOHCH_2OR\right]_n OCH_2\underbrace{CH-CH_2}_{O}$$

A one-to-two combining ratio of these ingredients should lead to the diglycidyl ether as shown in equation I. A one-to-one combining ratio can lead to a high molecular weight linear thermoplastic poly-bisphenol-A (1,3-glyceryl) ether as shown in equation II. The latter reaction proceeds by way of an initial formation of the monoepoxide ether. This epoxide in turn couples to the active hydrogen of phenolic hydroxyl group. As n in equation II increases from zero to three or four, the epoxy prepolymer changes from a light syrupy consistency to a low melting glassy resin. When n exceeds a hundred the product is tough thermoplastic molding compound.

Other epoxy resins are made by reacting epichlorohydrin with low molecular weight phenol-formaldehyde resins. Still other versions are produced by epoxidizing unsaturated linkages in low molecular weight compounds such as fatty esters and polydines.

Multiple substituted epoxy compounds are combined with reactive species, fillers, and catalyst and used for coating, impregnating, or molding purposes. Cure can be effected at room temperature with appropriate catalysts.

Thermal curing is preferred if the end product is expected to maintain properties and operate at elevated temperatures. Aliphatic polyamines are frequently used as low temperature reactive catalysts. Aromatic acid anhydrates are commonly used for thermal curing systems. Actual curing, chain extension and branching to form infinite networks occurs by a variation of the chemistry illustrated in equation II.

Epoxy resins find broad application in coatings, adhesives, composites, and potting and molding compounds. General properties include chemical and thermal-oxidative resistance, excellent adhesion to a variety of substrates, and an excellent balance of mechanical properties over a wide temperature range.

LINEAR VISCOELASTICITY

When one progresses from the foregoing qualitative discussion of structure-property relationships to the quantitative specification of mechanical properties, the most convenient point of departure into this large and complex subject is provided by the topic of "linear viscoelasticity". Linear viscoelasticity represents a relatively simple extension of classical (small strain) theory of elasticity. In situations where linear viscoelasticity applies, the mechanical properties can be determined from a few experiments, and can be specified in any of several equivalent formulations[11].

The accurate applicability of linear viscoelasticity is limited to certain restricted situations: amorphous polymers, temperatures near or above the glass temperature, homogeneous, isotropic materials, small strains, and absence of mechanical failure phenomena. Thus, the theory of linear viscoelasticity is of limited direct applicability to the problems encountered in the fabrication and end-use of polymeric materials (since most of these problems involve either large strains, or crystalline polymers, or amorphous polymers in a glassy state, or failure phenomena, or some combination of these disqualifying features). Even so, linear viscoelasticity is a most important subject in polymer materials science--directly applicable in a minority of practical problems, but indirectly useful (as a point of reference) in a much wider range of problems.

In an uncrosslinked amorphous polymer, above its glass temperature, the molecular chains are continuously wriggling from one conformation to another. If a mechanical stress is imposed on such a system of wriggling chains, it can respond in three distinct ways: (1) instantaneous elastic response; (2) retarded (conformational) elastic response; (3) viscous flow. Actually, in order to fit experimental data adequately, the retarded elastic element must be expanded into a whole series of such elements some with shorter and some with longer response times. The local "kinkiness" of the chains can be straigntened out (by stress) more rapidly than can the larger scale convolutions. The time scales of the various retarded elastic contributions range over many orders of magnitude from the fastest to the slowest.

In spite of these complications, the viscoelastic response of an amorphous polymer to small stresses turns out to be a relatively simple subject because of two helpful features: (1) the behavior is linear in the stress, which permits the application of the powerful superposition principle; (2) the behavior often follows a time-temperature equivalence principle, which permits the rapid viscoelastic response at high temperatures and the slow response at low temperatures to be condensed in a single master curve.

The superposition principle makes it possible to calculate the mechanical response of an amorphous polymer to a wide range of loading sequences from a limited amount of experimental information. Thus, from a single complete creep curve in pure shear or pure tension at a single load, it is possible in principle to calculate the response to combined stresses and time-dependent stresses (e.g., sinusoidal). Going still further, problems involving non-homogeneous time-dependent stresses in viscoelastic objects can be solved by means of the superposition principle. The two common types of boundary-value problems in elasticity theory (surface forces or surface displacements specified) generalize simply to the analogous viscoelastic problems (surface forces or displacements specified as functions of both position and time)[12].

The time-temperature equivalence principle makes it possible to predict the viscoelastic properties of an amorphous polymer at one temperature from measurements made at other temperatures. The major effect of a temperature increase is to increase the rates of the various modes of retarded conformational elastic response. This appears as a shift of the creep function along the log t scale to shorter times. A secondary effect of increasing temperature is to increase the elastic moduli slightly, since an equlibrium conformational modulus tends to be proportional to the absolute temperature[13].

By use of the time-temperature equivalence principle, the viscoelastic response of a given polymeric material over a wide temperature range can be accommodated in a single master curve. And by use of the superposition principle, this master curve can be used to estimate the time-dependent response to time-dependent stresses in simple tensile or shear specimens or to non-homogeneous time-dependent stresses arising in stressed objects and structures.

The relationship between molecular structure and viscoelastic properties involves both chemical composition and molecular architecture. The short-time (low temperature) behavior is relatively insensitive to molecular architecture, but master creep curves for different architectures diverge strongly at long times (high temperatures). The curve for a network polymer approaches a limiting asymptote, corresponding to equilibrium rubber elasticity; that of a linear polymer increases to infinity in a limiting steady-state viscous flow. The equilibrium rubber modulus is related to the density of crosslinks. To a first approximation, $G = K \cdot T \cdot \nu$, where ν designates crosslink density. In the vicinity of the gel point, Flory showed that it was necessary to correct for the wasted dangling tails which are attached to the network but cannot carry load at equilibrium[14]. Likewise, the melt viscosity of a linear polymer is strongly dependent upon chain length. A log-log plot of melt viscosity versus molecular weight commonly exhibits two straight-line sections, with a slope of unity or somewhat higher in the low molecular weight section and a slope of about 3.4 in the high molecular weight section[15]. The change in slope has been attributed to the onset of molecular entanglement[16].

At a given temperature, two polymers of similar architecture but different compositions exhibit creep curves of similar shape, but different locations along the log-t axis. When compared at "corresponding" temperatures, relative to their respective glass temperatures, their behaviors are very similar.

In a crude sense, the viscoelastic properties of a given polymer can be correlated with two numbers--one which reflects its chemical composition and one which characterizes its molecular architecture. The value of T_g conveniently serves the first role. The molecular architecture of a linear polymer can be roughly specified by the average chain length; that of a network polymer by the network density, or by the average molecular weight between crosslinks. Precise correlation of properties with structure must, of course, go deeper than this: molecular weight distribution must be considered; also, in a polymer such as poly(octyl methacrylate), the alkyl side group not only influences T_g, it also occupies space, and reduces the number of chains per unit volume. Ferry has considered such matters in detail[17].

Overall, the regime of linear viscoelasticity is characterized by reasonable success in establishing structure-property relationships. The properties themselves are unambiguously and simply specifiable. The relevant structural features are largely recognizable aspects of molecular structure. Molecular theories exist which provide a bridge between the molecular structure and the macroscopic viscoelastic properties.

LARGE STRAIN RUBBER ELASTICITY

The equlibrium small-strain elastic behavior of an "incompressible" rubbery network polymer can be specified by a single number--either the shear modulus G or the Young's modulus E (which for an incompressible elastomer is equal to 3G). This modulus being known, the stress-strain behavior in uniaxial tension, biaxial tension, shear, or compression can be calculated in a simple manner. (If compressibility is taken into account, two moduli are required: G and the bulk modulus B.) The relation between elastic properties and molecular architecture becomes a simple relation between two numbers: the shear modulus and the crosslink density (or the crosslink density corrected for the dangling tails). There can be some ambiguity as to how closely the "effective" crosslink density (calculated from the elastic modulus) approaches the "chemical" crosslink density (estimated from some chemical measure of crosslinking); however, in many elastomers the "chemical" crosslink density is not known with sufficient accuracy to make this a major concern.

When one proceeds to large elastic strains, the problem becomes more complex. The stress-strain relation in uniaxial tension becomes non-linear. It could be linearized, by a proper choice of the measure of deformation and the measure of stress, but a satisfactory treatment must also be consistent with the multi-axial large strain elastic behavior. One general approach to this problem has been through the use of a strain energy function W[18]. This is a scalar function of the three extension ratios, λ_1, λ_2 and λ_3. If W (λ_1, λ_2, λ_3) is known, the deviatoric stresses s_1, s_2 and s_3 can be calculated (as functions of λ_1, λ_2 and λ_3). The problem then becomes that of finding the proper form of the scalar function W (λ_1, λ_2, λ_3). Various choices have been suggested and tested. One of the most popular is the Mooney-Rivlin equation, which introduces a second elastic parameter. For uniaxial tension, the Mooney-Rivlin equation can be written:

$$\text{True Stress} = 2\ C_1 (\lambda^2 - \frac{1}{\lambda}) - 2\ C_2 (\lambda - \frac{1}{\lambda^2}),$$

corresponding to a strain-energy function of the form:

$$W = C_1 [I_1 - 3] + C_2 [I_2 - 3],$$

where I_1 and I_2 are invariants of the strain tensor.

A multi-parameter property equation calls for a multi-parameter structure specification. As one attempts to go beyond the effective crosslink density (corrected for dangling tails), it becomes difficult to identify the precise structural features responsible for the observed elastic properties. Some of these structural features are probably related to network topology. When crosslinks are introduced into a strained polymer, or in a solvent-swollen state, the resulting network has different properties from a network formed in an unstrained, unswollen condition--even if average molecular weight between crosslinks is the same[19]. No structure specification, couched only in terms of the connecting chains as network elements, is likely to capture the significant differences among such networks. An adequate structure specification probably must involve the closed loops of the network and their topological patterns; such aspects of structure are very difficult to establish[20].

NON-NEWTONIAN FLUIDS

At sufficiently high temperatures, a linear polymer behaves as an elastic fluid. At very low stress levels, the stady-state flow behavior is Newtonian; shear rate is directly proportional to shear stress. At higher stress levels, the elastic component of deformation contributes large elastic strains. The chain molecules are appreciably oriented by the flow process. Not only is there a transient elastic effect during the approach to steady flow and following cessation of flow, in addition, the molecular orientation strongly affects the steady-state relation between shear stress and shear rate. In the low-shear region, this steady-state behavior can be expressed by a constant-- the "zero-shear" viscosity (or its reciprocal, the fluidity). In the high-shear region, a non-linear function is required to specify the relation between shear stress and shear rate. This can be formulated in various ways*:

$$\begin{aligned} \dot{\epsilon} &= f(\tau) \\ \tau &= F(\dot{\epsilon}) \\ \text{or} \quad \tau &= \eta_{app}(\dot{\epsilon}), \end{aligned}$$

with η_{app} a non-linear function of $\dot{\epsilon}$ or τ. By symmetry, $f(\tau)$ must be an odd function--i.e., $f(-\tau) = -f(+\tau)$.

A power law expression provides a useful approximation to the flow curves for many molten polymers over a fairly wide range of shear rate[21].

$$\begin{aligned} \dot{\epsilon} &= k\tau^n \\ \text{or} \quad \tau &= K\dot{\epsilon}^m \end{aligned}$$

As written above, the power law does not satisfy the requirement of being an odd function. If negative values of $\dot{\epsilon}$ and τ are to be accommodated, the expression should be written in terms of absolute values:

$$|\dot{\epsilon}| = k\,|\tau|^n .$$

The steady-state flow behavior is not only nonlinear, it also is characterized by the development of normal stresses which are completely absent in a simple Newtonian fluid. Thus, a steady shear flow in the x-y plane, $\dot{\epsilon}_{xy}$, not only leads to a (nonlinear) shearing stress, τ_{xy}, but also to normal stresses σ_{xx}, σ_{yy}, σ_{zz}. Associated with these normal stresses are many

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* ϵ = strain
$\dot{\epsilon}$ = strain rate
τ = shear stress
η = viscosity

distinctive phenomena exhibited by polymeric fluids, such as the Weissenberg effect, where a polymer being stirred by a turning shaft tends to climb up the shaft instead of being thrown outwards by centrifugal action[22].

Thus, non-Newtonian polymeric fluids differ from simple Newtonian liquids in several ways: they exhibit transient effects in approaching steady-state flow; the steady state flow is nonlinear; and it is accompanied by normal stress effects. Consequently, a number of parameters are needed to specify the fluid properties. The relation of these parameters with molecular structure is only partially understood; but it is clear that the form of the molecular weight distribution and the degree of brancing of the chains, as well as the average molecular weight, must be considered. The structure-property relationships in this melt-flow regime are most important with respect to the efficient melt processing of thermoplastic polymers. This supplies a strong incentive to the development of more complete understanding of melt properties, molecular structures, and their interrelationships.

BEHAVIOR OF GLASSY AMORPHOUS POLYMERS

At very low strain levels, a glassy amorphous polymer behaves as a simple linear elastic solid, with a high Young's modulus (e.g., 4×10^{10} dynes/cm^2). When forced beyond this linear regime, a variety of non-linear, irreversible responses can occur: macroscopically brittle fracture; shear yielding (either uniform or localized); crazing; or some combination of these[23]. The stress level at which onset of any of these modes of response occurs depends upon many variables; the molecular structure (both composition and arcitecture); temperature; geometrical character of the stress rate of loading; contact with deleterious environmental agents; etc. Change in these variables can result in a switch from one mechanism of response to another.

Consider first the geometrical character of the stress. A multi-axial stress can be characterized by the three principal stresses S_1, S_2, S_3, listed in descending value. Shear yielding depends primarily upon the difference between S_1 and S_3. The Tresca yield condition, $S_1 - S_3 = Y$, (applicable to metals), has been modified for polymers (for which the shear yield stress Y increases with hydrostatic pressure[24].

The onset of crazing follows a completely different stress criterion, as reported by Sternstein[25]. Crazing is favored by high tensile stress, and a positive mean normal stress. Brittle fracture follows still another stress criterion. The mode of response to a particular type of stress depends upon which critical threshold is first crossed.

The shear yield stress depends upon temperature and strain-rate. So also do the stress levels for crazing and fracture but to different degrees. Thus, a change in temperature, or in strain-rate, can shift the mode of response[26].

The molecular mechanisms of these various responses, and their relationships with structure, are only partially understood. One thing, however, is certain, that we must go beyond molecular structure and consider supramolecular structure as well. The critical stress levels for yielding, crazing, and fracture depend strongly (and differently) upon the molecular orientation of a specimen. In the case of polystyrene at room temperature, uniaxial orientation can provide a marked increase in tensile strength, toughness, and craze resistance in the direction of orientation, and a marked loss in these properties in the transverse direction[27]. Biaxial orientation can confer strength and toughness in all directions in the plane[28].

BEHAVIOR OF CRYSTALLINE POLYMERS

Crystalline polymers, when forced beyond a limited linear regime, can also exhibit a variety of irreversible nonlinear responses to stress. Again, the mechanical behavior depends not only upon molecular structure, but also upon supramolecular structure--morphology and orientation. A given polymer can exhibit many different kinds of morphology, depending upon the history of temperature and stress encountered in processing. Among the recognized morphologies--each with its own distinctive pattern of properties--are the following: (1) Spherulitic morphology (commonly developed when a polymer crystallized from an unstressed melt)[29]; (2) Drawn fibrillar morphology (developed when a spherulitic polymer is stretched below its melting point and the original lamellar crystallites are fragmented and rearranged into an oriented fibrous structure)[29]; (3) "Shish-kebab" morphology (a different highly oriented morphology which develops when an orientated melt is crystallized[30]; (4) Extended chain crystals, "ECC" (which can be formed when polymer crystallizes under high hydrostatic pressure, or a crystalline polymer is annealed under pressure)[31]; (5) Oriented extended chain crystals as in high modulus fibers[32]; (6) "Accordion" morphology or "hard-elastic" fibers (formed by appropriate sequences of tensile stress and temperature[33 34]; (7) Various intermediate morphologies[35].

For a given polymer, the mechanical properties--modulus, tensile strength, yield stress, etc.--can show orders of magnitude differences in these various morphologies. And molecular structure influences properties--both directly and also indirectly as it influences the development of a particular morphology[36].

In spite of the above diversity of oriented crystalline morphologies, Samuels has shown that the structural state can sometimes be adequately characterized by the crystalline and amorphous orientation factors[37]. For polypropylene samples prepared with different draw ratios, draw temperatures, shrinkage temperatures, etc., simple property correlation with these two orientation factors was observed. "... these results suggest that different fabrication processes are simply different paths along which the sample is moved to equivalent structural states. Thus, general structure-property correlations are achieved by concentrating on the final structural states of the sample and not on the path by which that state was reached." Where applicable, this is a most useful approach; however, when radically different frabrication processes and radically different morphologies are compared, the definition of "structural state" must include more sbutle features than the crystalline and amorphous orientation factors.

In addition to the degree of crystallinity and the orientation of crystalline and amorphous regions, the shapes and sizes of the regions can be significant structural features, which can influence the way stress is distributed between the various regions.

A number of models have been proposed to attempt to account for this distribution of stress. For example, the model proposed by Reuss[38] assumes that each region sees the same stress while that proposed by Voight[39] assumes that each region sees the same strain. These two models represent the two extreme possibilities and it can be shown that while neither of these can be strictly correct all possibilities lie between these two extremes.

An interesting model is that proposed by Tsai and Halpin which uses a semi-empirical equation with a single parameter, ξ , called the contiguity parameter which determines the way stress is distributed[40]. When $\xi = 0$ the equation reduces to the Reuss model and when $\xi = \infty$ it yields to the Voight model. For intermediate values of ξ it can reproduce all other models which have been proposed (e.g., Takayanagi[41], Kerner[42], etc.). The Tsai-Halpin equation originated in the theory of composites where ξ could be quantitatively related to the length to diameter ratio of a fiber-reinforced composite. Halpin and Kardos have extended the concept to semi-crystalline polymers where ξ becomes a measure of the morphology of the crystalline regions[43]. In order to characterize completely the mechanical properties of a semicrystalline polymer (or any two-phase system) one needs to know, in addition to the properties of each phase, the following three factors: (1) crystallinity; (2) orientation (of any anisotropic region); and (3) contiguity (how stress is distributed). Numerous methods are available for measuring or estimating the first two of these factors, but contiguity is a relatively new concept and as yet there exist no methods for directly measuring the contiguity factor, ξ.

Although the contiguity concept is relatively new, the fact that the distribution of stress depends upon the size and shape (i.e., morphology) of the various regions has long been recognized. However, to relate morphology quantitatively to the distribution of stress has required the assumption of a model. The most common model is probably that of Takayanagi[41]. Using this model one can calculate a value for the contiguity, ξ, from the average dimensions of the crystalline regions. To gain some feeling for how ξ varies with morphology one notes that long fibrous crystals have a high value of ξ, while lamellar crystals have $\xi < 1$. A $\xi \rightarrow \infty$ would correspond to crystals with small noncrystalline regions completely embedded within them while $\xi \rightarrow 0$ corresponds to lamella-shaped crystals completely surrounded by noncrystalline regions[42]. It is also apparent that size and shape alone cannot completely determine the contiguity since the distribution of stress will also be affected by the way the regions are connected to each other.

The contiguity concept provides a new look into the potential properties of polymeric materials. In the case of polyethylene, for example, the elastic moduli of the crystalline regions can be calculated from first principles[43], and those of the noncrystalline regions estimated experimentally[44]. Thus, it becomes possible to calculate average moduli as a function of crystallinity, orientation, and contiguity and to compare these calculated values with experimentally measured results[45]. With but a few notable exceptions all observed values correspond to a contiguity of zero. The exceptions are those few cases where polyetheylene has been processed into filaments with what are believed to be extended chain crystals[46, 47]. Thus, it would appear that for the most part one can use the Reuss model with $\xi = 0$ for the distribution of stress. However, it is also clear that the mechanical properties of all polymers can be significantly improved if they can be obtained in a morphology with $\xi > 0$. The extent of improvement available is one to two orders of magnitude in elastic modulus. That this is not an unreasonable estimate can be seen if one considers that in an amorphous or semi-crystalline polymer, the initial deformation (which determines the modulus) is accomplished by bond rotation. If the contiguity of the specimen can be increased so that deformation requires bond bending or bond stretching, then the modulus can be increased one to two orders of magnitude.

An extreme example of oriented crystalline morphology and consequent tensile properties is provided by the aromatic polyamides[48]. The polymer molecules are highly rigid extended chains. In solution, they can spontaneously assume parallel orientation to form a "liquid crystal" or mesophase. When such liquid-crystal solutions are spun into fibers, the resulting fiber morphology leads to extremely high modulus and strength[49].

INTERACTION MATRICES

M. L. Williams and F. N. Kelley have introduced the concept of an interaction matrix to summarize the relationship between polymer structure and engineering properties[50].

In such a matrix, molecular parameters are represented by the rows, and engineering parameters by the columns. The matrix elements are labeled S, M, N, or U, to indicate interactions which are "strong", "moderate", negligible", or "unknown"; alternatively, when possible, quantitative evaluations may be employed.

One example of an interaction matrix presented by Williams and Kelley deals with the relaxation modulus, which can be approximated by the five-parameter equation:

$$(1) \qquad E_{rel}(t) = E_e + \frac{E_g - E_e}{[1 + (t_r/\tau_o]^n}$$

where E_e and E_g are the equilibrium rubbery modulus and the glassy modulus; τ_o is the characteristic time, and t_r is the temperature-reduced time ($t_r = t/a_T$), and a_T is a temperature dependent shift factor. The matrix which shows how these mechanical deformation parameters are related to polymer structure is presented as Table I.

Williams and Kelley also presented an interaction matrix for viscoelastic fracture. They used the modified Griffith critical stress criterion:

$$(2) \qquad \sigma_{cr} = \sqrt{E_{rel}(t/a_T) \cdot \gamma_c(t/a'_T)/a}$$

where E_{rel} (the relaxation modulus) and γ_c (the cohesive fracture energy) are both functions of temperature and time, and a is the initial flaw size. They represent the time-temperature dependence of γ_c by a five-parameter equation:*

$$(3) \qquad \gamma(t/a_T) = \gamma_e + \frac{\gamma_g - \gamma_e}{[1 + t/a'\tau_o]^{n'}}$$

The dependence of the fracture parameters of equation 3 on molecular structure is presented in the interaction matrix of Table II.

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* γ_e = fracture energy - equilibrium

γ_g = fracture energy - glassy

TABLE I

Interaction Matrix for Relaxation Modulus

	Modified Power Law Parameters				
Molecular Characteristics	E_g	E_e	τ_o	n	T_g
Crosslink Density	N	S	N	M	N
Chain Stiffness	N	N	U	M	S
Monomeric Friction Coefficient	U	N	S	U	S
Solubility Parameter	M	N	U	U	S
Molecular Weight	N	S	N	N	S
Heterogeneity Index	N	N	M	N	M
Molecular Weight Between Entanglements	N	S	N	N	N
Degree of Crystallinity	N	S	S	S	N
Volume Fraction of Filler	N	S	M	S	M
Volume Fraction of Plasticizer	N	S	S	N	S

U = Unknown, N = Negligible, M = Moderate, S = Strong

TABLE II

Relaxation Modulus for Viscoelastic Fracture

	Modified Power Law Parameters				
Molecular/Microstructural Characteristics	γ_g	γ_e	τ_o	n	T_g
Crosslink Density	M	S	N	M	M
Chain Stiffness	N	M	U	M	S
Monomeric Friction Coefficient	U	U	S	U	S
Solubility Parameter	S	M	U	U	S
Molecular Weight	N	S	N	N	S
Heterogeneity Index	N	N	M	N	M
Molecular Weight Between Entanglements	N	S	N	N	N
Degree of Crystallinity	U	S	S	S	N
Volume Fraction of Filler	S	S	M	S	M
Volume Fraction of Plasticizer	S	S	S	N	S

SUMMARY

The structure-property relations of polymers include the dependence of T_m and T_g on molecular structure, and the quantitative stress-strain-temperature-time behaviors exhibited in the various regimes relative to T_m and T_g. These quantiative behaviors, and their dependence on structure, are most completely developed in the regime of linear viscoelasticity (including the special cases of small strain rubber elasticity and low-shear-rate viscous flow). Large-strain elasticity and high shear-rate flow are somewhat more complicated, but are still correlated with molecular structure. In glassy amorphous polymers and crystalline polymers, supramolecular structure (e.g., orientation) as well as molecular structure must be considered in developing structure-property relationships. Since molecular structure is primarily established during polymerization, and supramolecular structure is established during subsequent fabrication operations, the mechanical performance of such polymers depends upon the conditions of fabrication as well as of polymerization.

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CHAPTER 5

STRUCTURAL DESIGN CONSIDERATIONS FOR POLYMERIC MATERIALS

INTRODUCTION

Conventional structural materials (metals, concrete, stone, glass and wood) are familiar to everyone, because of their widespread use and because they have been available for long periods of time. Their advantages and limitations are well known, information about them is easily obtained, and rarely are they misapplied or used in fashions which are inherently inappropriate. Although service failures of these materials do occur, usually they are caused by exposure to unforseen conditions (excessive loads, for example) by manufacturing errors or defects or by inadequate maintenance of parts made of them[1].

The situation with plastics is different in several ways. As a class of materials they are comparatively new. The first synthetic high polymer was prepared about one hundred years ago and became commercially available thirty years later; it was not until the period from 1930 to 1940 that an industry began to emerge. Only within the past fifteen years has the plastics industry become mature in a substantive sense. Most of the plastics in volume use today are less than thirty years old and since their inception many have undergone frequent enough and significant enough modifications to render them even "younger" than that. There is considerable complexity in the spectrum of available plastic materials: homopolymers of many different types, copolymers, blends, mixtures, variously reinforced systems, composites, etc.* Hundreds of different formulations are produced commercially; it is not surprising that the non-specialist invokes the term "plastics" for all, and lets it go at that.

Despite this confusing complexity, it is possible to state some general principles about the structural use of plastics and then use these principles in the design of functional parts and systems. This is the purpose of this chapter. While this chapter will be confined to generalities, enough actual examples of structural plastics exist to make credible their capability in this respect. The Boeing 747 airplane contains nearly two acres of polymeric adhesive joint area, much of it located in structurally critical regions in the fuselage and aerodynamic control surfaces. Tens of millions of cars, trucks,

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*It will be noted that the large class of synthetic fibers is not discussed in this chapter. This is because for structural design, as understood herein, fibers are used to distribute stress, reinforce a plastic, or be a part of a laminate. Hence, fibers are taken for granted and are not specifically considered.

and buses are braked by linings adhered to the metallic shoes with polymeric glues; in a very real sense, the lives of most of us depend upon the performance of those bonds. Plastics are structural materials in every sense of the term, if they are used correctly.

WHY PLASTICS?

Confronted with a structural need, whether it is demanding or almost trivial, e.g., an air-to-air missile or a hair comb, the materials selection process begins in the designer's mind. At this point it is helpful to have a realistic perception of the characteristics of plastics, their attributes and their limitations.

Generally plastics are light with specific gravity not much different from 1.0. Most plastics are good to excellent thermal and electrical insulators. Many are transparent or translucent to visible light. They generally do not corrode or oxidize as do metals. Most are resistant to that ubiquitous solvent, water; but, virtually every plastic can be attacked by some agent, e.g., solvents, oils, greases, soaps, etc. It follows that care and selectivity must be used if such environments will be encountered by the part. Plastics usually perform better at the low end of the temperature scale than at the high. Embrittlement and glassiness occur somewhere in the range of -70°C to 95°C but because of softening it is not easy to obtain satisfactory long term performance above about 205°C with a low cost polymer.

For reasons directly related to their nature, it is attractive to use plastics if only a few or few hundred parts are needed or if hundreds of thousands or more are sought. This is because easy liquid-to-solid conversions are available for small quantities and quick, low cost, low energy consumption solid-to-melt-to-solid ones exist when large runs are planned. The importance of this fabricating flexibility cannot be over-emphasized since time and again this flexibility is the compelling rationale for using a polymeric material to make a part. It also facilitates the incorporation of reinforcing fibers or particles, the use of plastics as films, coatings and adhesives and the mixing of different kinds of plastics for unusual combinations of properties.

Except in the drawn fiber form, most plastics are low modulus materials; values range from 0.25 to 1.5 x 10^6 psi. Frequently this contributes to superior shock resistance and impact energy absorption; it also causes large deflections under moderate stresses. Strengths are not high (3-15,000 psi ultimate tensile strength) and are time and temperature sensitive with a few exceptions; indentation hardness and wear resistance also are low, unless intrinsic lubercication films or similar mechanisms are present. Most plastics will burn. A variety of fire retarding or inhibiting methods are available to reduce this sensitivity to burning and some highly fire-resistant specialized polymers do exist; but, compared to metals or ceramics, it must be recognized that many plastics are flammable and may produce smoke and toxic products when they burn[21]. On a weight basis plastics are comparatively expensive materials; their use as a direct weight to weight replacement for metals, glasses, or wood can rarely be justified by lower costs. If the comparison is made on a volume basis, the situation may become more favorable to plastics, especially if finished parts with complicated geometries or shapes can be melt formed or cast directly with plastics instead of machined and/or assembled with metals. Usually, however, a plastics application must be justified by the need for some inherent property or combination of properties--light weight, visible light control, fabricability, low conductivity, chemical resistance, etc.--instead of by lower costs. That such justifications are numerous is attested to by the 1975 sales of plastics in the U.S.: 10.3 million metric tons, with the major uses being appliances, building and construction, electrical-electronics, furniture, housewares, packaging, toys, and passenger cars[2]. (On a volume basis this would be equivalent to about 70 million tons of steel or 25 million tons of aluminum alloy.)

WHICH PLASTICS?

With literally hundreds of commercial formulations available, any attempt to identify a single one in the absence of a particular performance specification appears futile; no such attempt will be made here. Instead, general classes and characteristics will be presented toward the purpose of clarifying some guidelines which may be helpful in the selection process. For this, an arbitrary division into three broad categories: (1) elastomers; (2) glasses; and (3) crystalline polymers are used.

ELASTOMERS

By this category is meant polymeric materials which show elastic behavior in the "normal" temperature range of -45°C to 95°C. They are soft, have a very low modulus, stretch hundreds of percent before they break, and recover with more or less hysteresis from the deformation once the load is removed[3].

Polyisoprene, that was once available only from rubber trees, is now synthesized in commercial quantities and finds its greatest use in vehicle tires. Its tear or crack propagation resistance is raised to high levels by heavy loading of carbon black filler, its abrasion resistance is good, the wet-skid characteristics are superior and it shows the least temperature increase or heat build-up from hysteresis under cyclic loading. The presence of unsaturated double bonds makes it susceptible to ozone attack which cause surface embrittlement and leads to crack initiation; many common solvents attack and swell it but once molded into shape it cannot easily be reformed or reused.

Polybutadiene has many characteristics similar to those of polyisoprene but most of its properties do not reach quite the same desirable levels. In one respect it is very attractive, however, it can be copolymerized with styrene, a glassy plastic, to yield a variety of products which can range from very soft to very hard. They give a wide spectrum of physical properties at low costs.

Both polychloroprene (neoprene) and the acrylate rubbers have superior chemical resistance, especially to hydrocarbons and organic solvents, though neither is as strong or abrasion resistant as polyisoprene. The polyurethanes excel in abrasion resistance--with good solvent resistance; they too can be formulated to range from a glassy state to an elastomeric state, though processing them involves exothermic liquid reactions that are often difficult to control.

Butyl rubber is 'lossy', i.e., absorbent of mechanical energy until heated well above room temperature; but its barrier properties to air are outstanding. Like the polysulfide rubbers it can be formulated into sticky but stable compositions that are useful as sealants and gaskets for outdoor use.

Silicone-based elastomers exhibit great chemical resistance and have a wide useful temperature range. Unfortunately they are expensive and not very rubbery.

Recently, injection-moldable or thermoplastic rubbers of several different types have been developed; these promise to become more popular because of their greater fabricating speed and flexibility. They can also be recycled.

All the rubbers can be foamed or rendered cellular quite easily, for use in cushioning and furniture, and this use consumes large amounts of butadiene and urethanes every year.

GLASSES

Around room temperature polymeric glasses are stiff, hard and usually brittle[4]. Frequently transparent, they are often used for glazing or in applications where integral coloration by dyes or pigments enhances their shiny surfaces.

The thermoplastic glasses, i.e., acrylics, styrenics, cellulosics, polycarbonates, vinyls, and polyesters can be softened and melted repeatedly. This is advantageous since they mold well and easily, reproducing complicated shapes and patterns satisfactorily. Their inherent brittleness can be overcome by including rubber particles in the glassy matrix which cause it to craze, yield and flow appreciably before breaking; the impact resistance can be increased by orders of magnitude in this way[5]. If greater stiffness, strength and resistance to elevated temperature are desired reinforcing fibers may be mixed with the thermoplastics in ratios as high as 35% by weight, without destroying their moldability. Chopped, inorganic glass fiber is frequently used for this purpose.

The thermoset glassy plastics, i.e., epoxies, polyesters, phenolics, alkyds and silicones undergo but one molding experience in their history. Crosslinks are formed between proximate chain molecules; these inhibit any subsequent thermal flow of the materials. The thermosets can be generally used at higher temperatures than the thermoplastics but the dimensional changes accompanying final solidification are great enough to require filling them with inert particles or reinforcing fibers to prevent cracking during molding. The hardening and strengthening effects are beneficial in themselves as is the improvement in resistance to elevated temperatures. Usually these materials show superior resistance to water and chemical attack because of their crosslinked structure though solvents or softening agents can be found for virtually all of them[6].

CRYSTALLINE POLYMERS

In several important respects, crystalline polymers are unusual. They can be mixtures of ordered and disordered material, crystalline and amorphous, or of highly and poorly ordered phases. In many systems the extent of crystallinity can be controlled by changes in molecular architecture and, to a lesser degree, by processing conditions. Since the crystallites act like physical crosslinks, this enables variations in macroscopic properties (stiffness, yield strength, ductility, toughness, permeability, etc.) over wide limits, especially above the glassy brittleness temperature. Because the crystallites possess many possible slip mechanisms, such polymers usually are tough, impact resistant, submissive to cold drawing and orientation, and resistant to cyclic mechanical fatigue damage. Normally their chemical resistance is superior, with certain notable exceptions, but the crystallinity prevents optical clarity except in relatively thin films[7].

By far the most common crystalline synthetic polymers are the polyolefins. These are principally polyethylene and polypropylene, comprising about 40% of the plastics produced annually. Polyethylene becomes brittle at about 120°C (polypropylene at -20°C) and the crystallites melt around 130°C (polypropylene about 175°C). Thus, over a broad range, including room temperature, the materials are leathery, tough, flexible, and strong. Coupled with ease of melt processing, these attributes make the polyolefins useful for films, coating, extrusions and moldings. Their inherently low coefficient of friction and resistance to wear add further to their versatility.

Perhaps one of the most provocative developments in polymer technology at the present time involves crystalline plastics. By artful extrusion followed by further drawing attenuation of such polymers, or by other schemes, it has been possible to obtain fibers containing significant fractions of extended-chain crystallites in which the backbones of the molecules are comparatively straight and parallel to the fiber axis. Theoretical calculations, predict, and experimental observations support, that great stiffness and strength can be obtained in such microstructures. This results in properties directly competitive with or superior to our highest performance metal alloys. As controls on such processes improve and as their ramifications are explored, it seems certain that the next decade will produce exciting advances in this area[8, 9].

THE DESIGN PROCESS

The task of the designer is to bring forth a part or system that will perform the specified functions and which can be produced in the required quantities at acceptable costs. Often this requires judgment, estimates, or guesses in many areas, particularly with respect to service loads and conditions throughout the entire life of the part. Failure to foresee all of the significant service loads and conditions can produce unpleasant consequences. In this section primary attention will be given to structural design of plastic parts. Since such matters must be considered for almost all plastics products, the consideration will not be confined or constrained.

First comes identification of the essential function of the part. What must it do? A standoff insulator must separate the wire from the pole electrically; therefore the standoff cannot be conductive. A tank of drinking water must contain the water and be proof against corrosion. A glazing unit must transmit visible light. Protective cushion packaging must absorb mechanical shocks. Pistons in an automobile engine must transmit forces at temperatures near the combustion point of the fuel-air mixture. If the "must function" is not met, the whole exercise is without meaning.

Next comes the question, how many? If only a few parts are needed, relatively cumbersome and inefficient methods of fabrication and assembly may be tolerable. If hundreds of thousands or millions of units of an article are sought, however, automated fabrication and assembly becomes imperative and economical. Few people care what a milk container looks like or is made of, as long as it holds the contents, is inexpensive, can be sterilized and is readily disposable. Involved directly in the question of quantity, however, is the material selection. Obviously automation and processing speed are not applicable to all materials to the same degree.

At this point, just on the basis of the essential function and the number of items required, the list of candidate materials already has been narrowed considerably. When the anticipated service requirements are factored in loads, environments, range of temperatures encountered, desired life, etc., and coupled with the consequences of failure, normally just a few candidates survive. Failures must be considered explicitly. If human life or safety are threatened, more stringent measures must be taken than if the milk container simply leaks. If a container is pressurized, one containing a carbonated beverage, for example, then an explosive failure can take place and people can be injured. The detailed design of the container and the material of which it is made become much more critical, as do inspection and surveillance procedures.

For the purpose of this discussion, let us assume that the foregoing factors combine to lead to the choice of a specific plastic for the part. Another series of questions must be answered as fully as possible:

(1) What forces and deformations will be imposed upon the part in normal use? What kind and degree of abnormal use must also be sustained? Are the forces (or deformations) invariant with time or will their characteristics change periodically? If they change periodically do they do so in a repetitive or random manner? Are the forces uniquely directed such that material anisotropy would be advantageous or would it be detriment if it arises from the fabrication process?

(2) Is the part's function stiffness or strength controlled? In other words, must it simply sustain the imposed loads without breaking, as an automobile tire, or must it not deflect too far in a fashion similar to a floor or a bridge which should not sway too much as one walks on it?

(3) What is the range of temperatures over which the part must perform? Are temperature variations likely in service and will they be such as to induce additional stresses or deformations in the part? How often and how rapidly will they occur?

(4) What environments will the part encounter in normal service? Will reactive liquids or vapors contact it continually, intermittently, rarely, never? Will it be exposed to water, either fresh, salt or brackish? Will variations in the concentration of such agents occur in the service environment, such as wetting and drying? How often?

(5) Is the appearance of the part important to its satisfactory function? Must the surface remain unchanged and the color fixed? Is renewal of the surface permissible and anticipated? How much degradation due to weathering or sun exposure can be tolerated?

(6) If mechanical failure occurs, if the part breaks, should it do so slowly and provide some warning, by slow growth of a visible crack, or is rapid, brittle fracture acceptable? Is high fracture toughness, insensitivity to local damage such as scratches, notches and holes, required for satisfactory performance?

(7) How will the part be fabricated? Will the method produce significant effects such as orientation, residual stresses, voids, shrinkage marks, surface roughness or others which may affect the strength of the material? Can these effects be put to advantage? Is the part designed to optimize its production by the method chosen, utilizing the simplest tooling and the shortest cycle times possible?

(8) What happens to the part after it is made but before it is put into service? How is it handled, stored, shipped, assembled? Often this stage is found to be the most severe which is encountered by many parts and systems; the service requirements are moderate compared to the abuses of storage and/or assembly.

Structural design considers the forces (and deformations) imposed on the part and sections it or dimensions it such that excessive stresses and strains do not occur. Initially, linear elastic behavior of the material is assumed. Classical elasticity methods of analysis are used if the geometry is simple enough to make them appropriate[10]. If not, computerized finite element techniques are employed because of their versatility and power[11]. If neither is completely satisfactory, a model of the part must be constructed and measurement of the strains made in regions where analytical methods are not effective[12].

Once the stresses and strains have been determined, the viscoelastic behavior of the plastic must be recognized. There are two principal ways to do so. In the first, an experimentally established time-dependent modulus is used to account for delay effects, and successive solutions are found, as before, using the time-changed value of the modulus to monitor the behavior of the part. (If loads and stresses are the independent variables, the creep modulus is used; if imposed deformations and strains are independent, then the relaxation modulus is appropriate. They are not the same for any single material.) By this procedure a series of successive "pictures" of the part may be obtained, showing its gradual change of size and shape as time passes. The modulus values used should be for the temperature of service. If the temperature changes, a different modulus-time curve may be required; to a first approximation, the effects are simply additive so they can be estimated quite readily. If the stress field is complex and multidiamensional, the usual case in reality, it is assumed that uniaxial behaviors are valid, that no interactions occur, and that the effects are superposable. Experience shows these assumptions to be true in general except for composites[13].

The second technique is more complicated but more precise. It requires an analytical characterization of the viscoelastic behavior of the material, usually in the form of a constitutive equation which relates stress, strain, time and temperature. The part is analyzed as if it were composed of a linearly elastic material. Then by the so-called correspondence method, the elastic constants in the solution are replaced by viscoelastic operators and the resultant transformed equations are solved to provide a time-dependent analysis of the part. When applied carefully, this technique is powerful and accurate unless non-linear viscoelastic behavior occurs. However, this is usually deduced from the size of the strains or deformations encountered[14].

Between these two methods, which might be viewed as the extremes, a number of other analytical procedures are available. Many of them use relatively simple analytical expressions for the time-dependent modulus or incorporate the concepts of a rate process into the calculation of deformations and strains. When restricted to a particular material-product combination, e.g., pressurized poly(vinyl chloride) pipe, they can be refined empirically to a high degree of accuracy and usefulness[15,16].

Another concept of great utility in the structural design and analysis of plastic parts is the time-temperature superposition principle. Stated simply, this postulates that long time behavior at one temperature can be observed in shorter times at a higher temperature and that predictions in the time-temperature domain can be made by suitable extrapolative methods. Initially conceived for deformation phenomena, it also applies to the strength behavior of many plastics and is a very useful tool for designers[17].

The strength of all plastics is time sensitive. Under a steady tensile load the breaking stress decreases as the loaded time increases. This characteristic, known as "static fatigue" is exhibited by many other materials and is not peculiar to polymers. However, the sensitivity of the effect to environmental agents is very marked with plastics, apparently because many liquids and vapors can plasticize the materials and facilitate chain-chain slippage which leads to crazing or cracking. Many of the "stress cracking agents" occur commonly. Alcohol, water gasoline, soaps and detergents, vegetable oils, animal fats, milk, butter, perspiration and organic cleaning fluids are among the agents known to moderately or greatly reduce the stress-rupture resistance of numerous frequently used plastics. Usually, if it occurs, the effect is serious enough for a given polymer to require an explicit remedy. Among the possibilities are: to provide a barrier to the agent, reduce the stress in the part, remove the offending agent from the environment or change the composition of the plastic to lessen the solubility of the agent in it. Sometimes orientation of the molecular structure also improves its environmental stress cracking resistance, but this must not be merely a skin effect or no benefit is gained. The producers of plastic materials have collected a great amount of data on the general cracking phenomenon, as related to their own products. Good information generally is available from them or from the technical literature[18].

Alternating stresses and deformations also produce damage and loss of strength; however, the severity of the reduction varies greatly with the plastic. For example, polypropylene is so resistant to cyclic fatigue that "infinite life" hinges are fabricated of it while glass fiber reinforced polyesters or epoxies can lose half their strength after a few hundred thousand cycles because of brittle matrix cracking and damage to the fibers. As with the static case, environmental effects operate here also, though not always to the same degree. A reasonable data base exists for the static case. The amount of available information on cyclic fatigue is not great and basic understanding of the mechanisms involved is less than complete. Much remains to be accomplished [19].

To recapitulate, the initial step in the structural design and analysis of a plastic part is to treat it as ideally elastic. Then concepts of a time-dependent modulus can be introduced or the correspondence principal utilizing viscoelastic operators can be employed. Other methods of intermediate complexity are available. A powerful tool for predictions of longtime creep and stress rupture behaviors is the time-temperature superposition principle.

Environmental factors must be considered, usually on the basis of empirical test data, to ensure that accelerated effects either do not occur or are accounted for in the design and dimensioning of the part. Finally, the consequences of failure must be evaluated just as comprehensively as possible. If life or safety is threatened, gross overdesign may be required, principles of redundancy may be invoked, one hundred percent inspection of parts could be required, and surveillance of the part in service might be specified.

PROTOTYPE DEVELOPMENT AND TESTING

Often much of the foregoing design and analysis process is condensed and replaced by prototype development and testing, either in hope of saving time and money or because the part is so complicated that the analytical process would not be rewarding. An empirical series of successive approximations is followed, starting from simplified calculations frequently influenced strongly by the fabricating capability available to the producer. Both the efficiency and effectiveness of the empirical approach depends heavily on the experience and judgment of the persons involved and the scope of the testing which is done. If both of these are of high quality, the process can produce good results, fast and cheaply.

Irrespective of the nature of the design process which is used, the part testing phase should be performed[22]. The ideal test is real life service since this encounters all the elements of use, and abuse, unforseen by the designer, but real life testing is difficult to monitor, expensive to control, and may be hazardous, either literally or commercially, if failures occur. For these reasons, simulated service tests under controlled conditions in the laboratory are usually preferred. Temperature cycling, load cycling, environmental exposures, creep tests, creep-rupture tests, static and impact strength measurements, exposure to simulated weathering, electrical performance--the variety of such tests is almost endless--but the basic idea is to evaluate the behavior of the part when used in a manner similar to that for which it is intended, under conditions subject to measurement and recording. Such tests often are ingenious in their simulation of service conditions, though this may be offset by the typical tendency toward order and programming characteristic of the technical person's approach. Despite this, simulated use tests are necessary and should be performed with enough replication and variety to make statistical analysis of the results valid. They also provide another useful function, that is to monitor the quality of the material used in the part and the consistency of the processing it undergoes in conversion to the final product[20].

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CHAPTER 6

POLYMER CHARACTERIZATION

HISTORICAL INTRODUCTION[1]

The characterization of polymers may be said in a sense to have begun with the recognition and demonstration of the high molecular weight and long-chain nature of these substances. There were a few even earlier characterization measurements on what is now recognized to be polymers, such as van't Hoff's early studies of osmotic pressure, but it was not until the work of Staudinger in the 1920's and 1930's that the nature of the polymer molecule was elucidated by a brilliant series of characterization studies. Staudinger recognized and studied the major molecular characteristics of polymers: their long-chain nature, their high molecular weight, and their molecular-weight distribution, as well as the physical nature of their partial ordering in the solid state.

Since Staudinger's time, the development of polymer characterization methods has advanced alongside the development of the synthesis and industrial use of polymers. As often happens, this development has occurred in a series of forward steps, each followed by a period of refinement, consolidation, and application. Using molecular-weight characterization as an example, the colligative methods and the chemical methods of end-group analysis for the determination of the number-average molecular weight were applied to polymers immediately after Staudinger's time. The next stage of development included light scattering and ultracentrifugation in the late 1930's and early 1940's, leading primarily to the determination of the weight-average molecular weight. At the same time x-ray diffraction was applied to the characterization of the crystal structure, degree of order, and orientation of semi-crystalline polymers.

What is now considered by many to be the most practical approach to the characterization of molecular-weight distribution came much later with the development in the 1960s of gel permeation chromatography (GPC), also known as liquid exclusion chromatography. At this time, also, the application of electron microscopy led to the current understanding of the morphology of semi-crystalline polymers. In addition, through these years techniques for the characterization of the physical properties of polymers were being developed, usually as the result of some industrial need.

APPLICABILITY OF CHARACTERIZATION METHODS

PITFALLS IN APPLYING CHARACTERIZATION TECHNIQUES

As a result of the development of many special characterization techniques for polymers and of the application to these materials of a large number of standard analytical methods, there is a wide selection of characterization methods from which to select those suitable for a particular system. But unfortunately, many available techniques are not applicable to all polymer systems. Again it is instructive to use molecular-weight characterization as an example.

All of the molecular characterization methods work rather well when applied to relatively simple cases, such as linear holopolymers readily soluble in relatively non-polar solvents at room temperature, and with moderate values of molecular weight and the breadth of its distribution. Likewise the physical characterization techniques can usually be understood as long as model systems are used.

However, in the real world the industrial use of polymers has led to interest in materials with higher and higher levels of performance. Such materials usually have more and more complicated molecular and supramolecular structures and, in direct consequence, less and less tractable properties for the application of characterization methods. The greatest challenges to the practitioners of polymer characterization today come from the need to understand these complications of structure associated with polymers of greatest current interest.

PERFORMANCE SPECIFICATION TESTING

As a result of these complications, those concerned with the use of polymers have most frequently had to resort to what are called performance specification tests. That is if a polymer performed satisfactorily for a given use or met presumed relevant, specifications based on the characteristics of a material known to perform satisfactorily, then it was acceptable. Although obviously many of the characteristics tested are relevant to the end use, the result has been the development of hundreds of such tests with little or no basic understanding of the type needed for design criteria. These tests, as described in the standards literature of all of the major industrial countries, are easily accessible to polymer specialists and perform well for the use intended. The difficulty comes in extrapolating them beyond the limited use for which they are intended; i.e., one can determine if a polymer meets a certain specification, but not if it will perform adequately in a given end use. Examples of the application of these standard tests are discussed in the case studies in Chapter 7.

SUMMARY OF CHARACTERIZATION TECHNIQUES

LISTING OF EXAMPLES

Early in the Committee's deliberations, it was recognized that a critical evaluation of existing characterization techniques would be desirable. Despite the usefulness of such a report, this was impossible within the time limitations, finances, and manpower available. The evaluation of even a single ASTM method or specification frequently takes years. Rather, it was felt that it would be appropriate to discuss, in this chapter, the Committee's view of the current state of characterization methodology and to gather examples of many of the newer techniques. Accordingly a request for brief descriptions of non-ASTM techniques was sent to: (1) all manufacturers of polymer testing equipment listed in the 1975 Modern Plastics Encyclopedia; (2) an appropriate person at each of twenty primary polymer manufacturers; and (3) ca. 4500 members of the American Chemical Society, Polymer Division and 600 members of the American Physical Society, High Polymer Division (appreciation is expressed to the latter two organizations for permission to use their membership lists).

Usable characterization technique descriptions were received from three of the equipment manufacturers, several of the polymer manufacturers, and ca. 75 American Chemical Society and American Physical Society members. These are listed by title and contributor in Appendix 6A, which is subdivided into the sections described in Table 1.

The full collection of complete descriptions is on file with the National Materials Advisory Board*. Several of the polymer characterization techniques listed in Appendix 6A have particular relevance to one or another of the case studies presented in Chapter 7, and these are reproduced in Appendix 6B.

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*National Materials Advisory Board, Commission on Sociotechnical Systems, National Research Council, 2101 Constitution Avenue, N. W., Washington, D. C., 20418 should be approached if it is desired to have access to the file. Under ordinary circumstances access will be granted by prior appointment on business days during regular working hours.

TABLE 1

SUMMARY OF POLYMER CHARACTERIZATION TECHNIQUES LISTED IN APPENDIX 6A

Technique Category		Number Listed
Chemical		11
Electrical		4
Mechanical		19
Molecular		14
Physical		12
Rheological		4
Spectroscopic		10
Thermal Property		11
Thermal Transition		10
Viscoelasticity		12
	Total	107

OTHER NEW CHARACTERIZATION TECHNIQUES

Along with the advances in science, during the last several decades, there has been a corresponding increase in the development and application of new analytical techniques and equipment. Many of these are summarized in the annual review of Mitchell and Chiu[2] and include Auger electron spectroscopy, molecular-beam interactions, optical rotary dispersion and circular dichroism, spin-echo NMR, nuclear quadrupole resonance Mössbauer scattering, ESCA, acoustic spectroscopy and thermoacoustic analysis. In addition, even in such an old technique as light scattering there are numerous new techniques made possible by the use of a laser as a source. Summarized recently by Kinsinger[3], these included Rayleigh-Brillouin and light beating spectroscopy. Thus, light scattering can now be used to characterize, in addition to molecular weight and size, concentration fluctuations, translational, rotational, self and mutual diffusion constants, critical phenomena, hypersonic velocity and sonic attenuation, diffusional processes, jump versus segmental motion, and rotational relaxations.

Appended to this chapter (Appendix 6-C) is a discussion in some depth of measurements of chain scission and the atomic and/or molecular occurrences associated with fracture.

PHILOSOPHY OF CHARACTERIZATION

DEFINITION

It is well documented in this report and elsewhere, and in fact it was the cause of the request for this report, that existing characterization methods are not meeting the needs of those concerned with the ultimate performance of polymer materials. The definition of characterization as given by the earlier Committee on Characterization of Materials in its 1967 report is here repeated: "Characterization describes those features of the composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use, and suffice for reproduction of the material".

According to the 1967 report one neither knew how to characterize polymers uniquely nor fully appreciated the lack of this ability. Almost ten years later, despite the increase in number of techniques, there has been little progress in most areas. The practical problem, however, is not so much the availability of characterization techniques but their application in an economically feasible, scientifically sound manner to the situation at hand.

SPECIAL DIFFICULTIES IN CHARACTERIZING POLYMERS

The reason for this lack of advance is that the characterization of polymers is inherently more difficult than that of other materials[4]. Polymers are at least as complex, if not more so, than other materials at every physical level of organization, from the helical conformation in chain folded single crystals to spherulite morphology. At the molecular level the complexities in configuration and sequence have no counterpart in the relatively simple groups of atoms forming the structural elements of metals or ceramics. Time dependent elastic and viscoelastic properties are especially important to polymers.

NEEDS AND ALTERNATIVES

One faces the horns of a dilemma. On the one hand, the need for better characterization is well demonstrated. Not only is much of the scientific literature in polymers based on inadequately characterized samples, but the procurement and utilization of a polymer material (by the Armed Forces, for example) with the assurance it will perform as expected cannot be insured if its basic characteristics are unknown or inadequately understood. Ideally it would be desirable to characterize all aspects of polymer structure in enough detail to predict its performance from first principles. It is doubted that this will be possible; and even if it were, it would not be economically feasible.

On the other hand, the current method of finding a satisfactory material for a given use and then expecting the supplier to always furnish the same material is equally unrealistic. Not only is it by no means certain that he will be able to do so, but apparently trivial changes in composition or the manufacturing process may lead to unexpected changes in properties. Related problems arise in obtaining a second source if the initial source ceases production (e.g., most polymer single crystal studies have been based on "Marlex" 6050, a resin that is no longer manufactured).

A COMPROMISE SOLUTION: SOME CONCLUSIONS AND RECOMMENDATIONS

The best solution calls for meaningful characterization, based on the selection, from all possible molecular and physical parameters, of those whose determination will insure the desired performance within the limits of current knowledge. The hope is that by appropriate compromise, adequate information can be obtained with an economically feasible amount of testing.

The success of this approach requires depth in knowledge of polymer science and of the characterization that serves as a base. Regrettably it is believed that this base does not now exist nor is it likely to develop unless the importance of this objective is recognized and steps taken to implement it. What is seen instead is that fundamental characterization is going out of style. Fewer laboratories (industrial, government, or academic) are practicing, developing or teaching the techniques of basic characterization or extending them to the more complicated cases which are becoming of greater interest. In molecular characterization, for instance, fewer laboratories are maintaining their skill in light scattering techniques, membrane osmometry, equilibrium ultracentrifugation, and others that are based soundly on thermodynamic principles. Even the instrumentation for these techniques is in some cases off the market or outmoded. The primary exception appears to be gel permeation chromatography. Even here it is frequently not realized that careful calibration is required if meaningful results are to be obtained, and that calibration samples require the application of fundamental thermodynamic methods for their characterization. Although obviously needed, modern equipment is not enough. Infinitely more needed are skilled persons capable of choosing the appropriate techniques, knowing both their limitations and applicability. The problem of finding support for appropriate educational programs to interest qualified trainees is the shared responsibility of industry, academia, and government granting agencies.

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Organic Polymer Characterization: Report
http://www.nap.edu/catalog.php?record_id=20350

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APPENDIX 6A

EXAMPLES OF POLYMER CHARACTERIZATION TECHNIQUES

(The original methods have been filed and are available for consultation in the office of the National Materials Advisory Board.)

TITLES AND CONTRIBUTORS

6A. 1 Chemical Techniques

6A.1.1 Pyrolysis Gas Chromatography Method of Analyzing Polymers, H. N. Ramaswamy, AZS Chemical Company

6A.1.2 Polymer-Solvent Interaction Parameters from Phase Equlibrium Data, R. L. Kruse, Monsanto Company

6A.1.3 Determination of Unreacted Monomers In Aqueous Emulsons of Interpolymers (by gas chromatography), P. Shapras and G. C. Claver, Monsanto Company

6A.1.4 Determination of Residual Monomers and Other Volatile Components in Styrene Based Polymers by Gas Chromatography, P. Shapras and G. C. Claver, Monsanto Company

6A.1.5 Density Gradient Centrifugation to obtain Information Regarding Compositional Distribution in Polymers, J. J. Hermans, University of North Carolina

6A.1.6 Diffusive Transport Through Membranes, E. Klein, Gulf South Research Institute

6A.1.7 Water Vapor Transmission Through Elastomers (Molecular Transport), Robert L. Buchanan, Tompkins Rubber Company

6A.1.8 Substrate Wetting Behavior of PTFE Resin Particles by a Combination of Scanning Electron Microscopy and Chemical Etching, N. E. Weeks and E. P. Otocka, Pratt & Whitney Aircraft

6A.1.9 Embrittlement of Externally-Stressed Polymers in an Active Environment, W. H. Haslett, Monsanto Company

6A.1.10 An Improved Variable Strain Bending Form for Determining the Environmental Craze Resistance of Polymers, W. H. Haslett, Monsanto Company

6A.1.11 Critical Strain for Environmental Stress Crazing or Cracking, Roger P. Kambour, General Electric Company

6A. 2 Electrical Techniques

6A.2.1 Electrostatic Charge Characteristics of Polymer Powders, Southeng Wu, E. I. duPont de Nemours & Co. (Inc.)

6A.2.2 Tribocharging Characteristics of Polymer Powders, Southeng Wu, E. I. duPont de Nemours & Co. (Inc.)

6A.2.3 Dynamic Dielectric Analysis of Polymers, Stanley A. Yalof, Tetrahedron Associates

6A.2.4 Continuous Titration of Ionisable Acids With a Differential Conductimetric Method. Its Application to Thermal Degradation of Halogenated Polymers and Copolymers, M.J.C. Beneugo and M. Bert

6A. 3 Mechanical Techniques

6A.3.1 Mechanical Properties in Polymers, Eloisa B. Mano and Teresa Keiko N. Fujiii, Universidade Federal do Rio de Janeiro, Brazil

6A.3.2 Mechanical Properties of Asphalt Materials, K. L. Jenua, MTS Systems Corporation

6A.3.3 Mechanical Properties of Elastomer Materials, K. L. Jenua, MTS Systems Corporation

6A.3.4 Rate Dependent Stress-Strain Properties of Polymeric Materials, K. L. Jenua, MTS Systems Corporation

6A.3.5 Fracture Mechanics Properties of Polymeric Materials, K. L. Jenua, MTS Systems Corporation

6A.3.6 Fatigue Properties of Polymeric Materials, K. L. Jenua, MTS Systems Corporation

6A.3.7 Mechanical Properties of Polymeric Materials Under Combined Mechanical Excitations, K. L. Jenua, MTS Systems Corporation

6A.3.8 Impact Strength of Polymers by Ball Impact Tester, T. M. Long Company

6A.3.9 The Driven Dart Impact Tester for Plastics, Victor A. Matonis, Monsanto Company

6A.3.10 Autographic Falling-Weight Impact Test, Henry Gonzalez, Jr., Tennessee Eastman Company

6A.3.11 Determination of Abrasion Resistance From the Time Dependence of Abrasion, Jan Bares, Xerox Corporation

6A.3.12 In-Plane Shear Strength and Modulus of Thin Polymeric Films, Wendell T. Jackson, Hexcel Corporation

6A.3.13 Polymer Deformation in Multi-Axial Field by Laboratory Film Stretcher, T. M. Long Company

6A.3.14 Mechancial Properties of Multi-Axially Stressed Film, T. M. Long Company

6A.3.15 High-Speed Tensile Behavior of Polymers, Albert F. Yee, General Electric Company

6A.3.16 Electrothermal Mechanical Analysis (ETMA) Stan Yalof, Tetrahedron Associates

6A.3.17 The Use of E, Young's Modulus, to Determine N, the Number of Hydrogen Bonds per cm^3, Effective in Carrying Stress in a Hydrogen-Bond Dominated Polymer Undergoing Unidirectional Tensile Strain, Alfred H. Nissau, Westvaco

6A.3.18 Sensitivity of the Temperature Dependence of Polymer Mechanical Properties to the Presence of Water, John F. Walters, Phillips Fibers Corporation

6A 3.19 Design Life Predictions Based on Combined Static and Dynamic Loading Strains, J. Nelson Knight, William R. Schlich, and Donald T. Willian, General Electric Company

6A. 4 Molecular Techniques

6A.4.1 Determination of Molecular Weight, Shape, and Deformability of Macromolecules by Means of Flow Light Scattering, W. Heller, Wayne State University

6A.4.2 Number-Average Molecular Weight by Elasto-Osmometry, J. J. Hermans, University of North Carolina

6A.4.3 Characterization of the Polydispersity of Polymers by Sedimentation Velocity Molecular Weight, Yvon Sicotte, University of Montreal

6A.4.4 Density Gradient Centerfugation to Obtain Information Regarding Molecular Weight Distribution, J. J. Hermans, University of North Carolina

6A.4.5 Molecular Weight Distribution and Branching in Polymers by GPC Viscometry and Low-Angle Laser Light-Scattering Photometry, A. C. Ouano, IBM Research

6A.4.6 Determination of Low-Molecular-Weight Polymers by the GPC-Universal Calibration Curve, J. B-son Bredenberg, Neste Oy, Finland

6A.4.7 Characterization of Oligomers by GPC, Walter Heitz, Marberg University, Germany

6A.4.8 Branching in Polymers (by GPC), Michael R. Ambler, Goodyear Tire and Rubber Company

6A.4.9 Determination of Grafted Chain Lengths and Frequency of Grafting In Grafted Polybutadiene Rubbers (by ozonolysis-GPC), Peter Shapras and George C. Claver, Monsanto Company

6A.4.10 Microgel and Macrogel Contents in Polymers (by filtration), Michael R. Ambler, Goodyear Tire and Rubber Company

6A.4.11 Chemical Composition Distribution of Copolymers by Cross Fractionation, Shinya Teramachi, Kogakuin University, Japan

6A.4.12 Heterogeneities of Copolymers and Homopolymers by Thin Layer Chromatography, Tadao Kotaka, Kyoto University, Japan

6A.4.13 Identification of Heterophase Components in Polymeric Materials (by swelling), Max Kronstein, Manhatten College

6A.4.14 "Iso-Ionic" Dilution to Determine the Intrinsic Viscosity of a Polyelectrolyte as a Function of the Concentration of Extraneous Salt, J. J. Hermans, University of North Carolina

6A. 5 Physical Methods

6A.5.1 Determination of Density of Solids by Density-Gradient Tube, B. W. Oliver, Jr., Tennessee Eastman Company

6A.5.2 Particle Size Analysis (by light scattering), R. J. Clark, Monsanto Company

6A.5.3 Structural Characteristics of Polymers Determined From Their Light Scattering Properties, Richard A. Farrell and Russell L. McCally, Johns Hopkins University

6A.5.4 Determination of Particle Size Distribution, Number Concentration, and Surface Area of Polymer Latex Suspensions by Light Scattering, Robert L. Rowell, University of Massachusetts

6A.5.5 Rapid Determination of Size Distributions in Colloidal Dispersions of Macromolecular Materials Having a Spherical Shape, W. Bergman and W. Heller, Wayne State University

6A.5.6 Determination of Polymer Particle Size Distribution in Latices by an Analytical Ultracentrifuge, Odd Palmgren, Norsk Hydro, Norway

6A.5.7 Refractive Index and Birefringence in Copolymers and Semicrystalline Polymers by Polarized Refractometry, Donald G. LeGrand, General Electric Company

6A.5.8 Porosity of Solid Polymers (by memory porosimetry), R. G. Quynn, FRL

6A.5.9 Interfacial Tensions Between Polymers and Surface Tensions of Molten Polymers by the Pendant Drop Method, Southeng Wu, E. I. duPont deNemours & Company (Inc.)

6A.5.10 Properties of Macromolecular Films of Polymers, Southeng Wu, E. I. duPont deNemours & Company (Inc.)

6A.5.11 Surface Tension (Surface Free Energy) and Polarity of Solid Polymers, Southeng Wu, E. I. duPont deNemours & Company (Inc.)

6A.5.12 Method for Examination of Polyester Chip for Degradation (by light microscopy), Paul J. Rau, Phillips Fiber Corporation

6A. 6 Rheological Techniques

6A.6.1 Melt Viscosity by Capillary Rheometry, E. J. Tolle, Imass Company

6A.6.2 Time-Temperature-Viscosity Characterization of Curing Thermoset Resins, Mark B. Roller, Mobil Chemical Company

6A.6.3 Prediction of Injection-Molding Behavior from Melt Rheology Data, Douglas P. Thomas, General Electric Company

6A.6.4 Rate of Gelation (Fusion) of PVC Samples by Analyzing the Sections of Helical Ribbon From an Extruder, Erik Odgaard, Norsk Hydro, Norway

6A. 7 Spectroscopic Techniques

6A.7.1 Crystallite Orientation or Planar Orientation of Crystal Planes in Crystalline Polymers by Wide-Angle X-ray Diffraction, Ryozo Kitawaru

6A.7.2 Elastic Modulus of Polymer Crystals by X-ray Diffraction, Ichiro Sakurada, Kyoto University, Japan

6A.7.3 Lamellar Orientation in Crystalline Polymers by Small–Angle X-ray Diffraction (Photographic), Phillip H. Geil, Case Western Reserve University

6A.7.4 Lamellar Orientation in Crystalline Polymers by Small–Angle X-ray Diffraction (Pole Figure), Phillip H. Geil, Case Western Reserve University

6A.7.5 Degree of Crystallite Orientation in Cellulose Fibers by X-ray Diffractometer, Joseph J. Creely, U. S. Department of Agriculture

6A.7.6 Determination of Trace Elements in Polymers (by x-ray fluorescence), Robert F. Rosenthal, Phillips Fibers Corporation

6A.7.7 Interlamellar Phase Transitions in Crystalline Polymers by IR Spectroscopy, John J. White, III, Battelle

6A.7.8 Orientation Measurements by Infrared Dichroism, Stuart L. Cooper, University of Wisconsin

6A.7.9 Structural Determinations of Flouropolymers by Carbon-13 NMR Spectroscopy, Madeline S. Toy and Roger S. Stringham, Science Applications.

6A.7.10 Determination of Tacticity in Polymeric Methacrylate Esters (by NMR), L. Guy Donaruma, California State University, Fullerton

6A. 8 Thermal Property Techniques

6A.8.1 Heat Capacities by Differential Thermal Analysis, Bernhard Wunderlich, Rensselaer Polytechnic Institute

6A.8.2 Heat Capacity of (Bio)Polymers at Low Temperatures (1-20° Kelvin), L. X. Rinegold, Drexel University

6A.8.3 Heats of Transition by Differential Thermal Analysis, Bernhard Wunderlich, Rensselaer Polytechnic Institute

6A.8.4 Thermal Expansion Coefficient, Robert A. Orwoll, College of William and Mary

6A.8.5 Thermogravimetric Analysis Connected to Gas Chromatography Analysis. Application to Thermal Degradation of Copolymers, J. Guillet and M. Bert

6A.8.6 Thermal Stability of Fluid Polymers Used as Liquid Phase in Gas Chromatography, Georges Guiochou, Ecole Polytechnique, Paris

6A.8.7 Identification of Elastomers in Tire Sections by Total Thermal Analysis, Anil K. Sircar and Trevor G. Lamond, J. M. Huber Corporation

6A.8.8 Photopolymerization (or Photoreaction) Rate Studies by Differential Calorimetry, Allan R. Shultz, General Electric Company

6A.8.9 Crystallinity of Polymers by Gas Chromatography, J. M. Braun and J. E. Guillet, University of Tronto

6A.8.10 Molecular Orientation in Amorphous Polymers by Heat Shrinkage, H. Heron, Technical University of Denmark

6A.8.11 Determining Glowing Combustibility in Thin Polymer Samples, A. Broido, U. S. Forest Service

6A. 9 Thermal Transition Techniques

6A.9.1 Transition Temperatures in Crystalline or Semicrystalline Samples by Differential Thermal Analysis, Bernhard Wunderlich, Rensselaer Polytechnic Institute

6A.9.2 Glass Transition Temperatures by Differential Thermal Analysis, Bernhard Wunderlich, Rensselaer Polytechnic Institute

6A.9.3 Modified Film Sample-Mounting Method for Thermo-Mechanical Determinations of Glass Transition Temperature (T_g), Harold D. Burks, NASA-Langley

6A.9.4 Estimate of the Glass-Transition Temperature of Polymer by Gas-Liquid Chromatography, Pe-Hwa L. Hsiung, College Park, Maryland

6A.9.5 Determination of T_g by Depolarization Microscopy (Thermo-Optical Analysis), S. Y. Hobbs, General Electric Company

6A.9.6 Glass Transition Temperature of Polymers by Gas Chromatography (Molecular Probe), J. M. Braun and J. E. Guillet, University of Toronto

6A.9.7 Heat Distortion Point as Measured on Purified Polymer by a Compression Molded Sample, R. W. Raetz

6A.9.8 Heat Distortion and Mechanical Properties of Polymers by Thermal-Mechanical Analysis, Alan T. Riga, Luberizol Corp.

6A.9.9 Torsional Pendulum and Torsional Braid Analyses of Polymers, John K. Gillham, Princeton University

6A.9.10 Transitions of Polymers by Positron Annihilation Lifetime Measurement, S. J. Tao, The New England Institute

6A. 10 Viscoelasticity Techniques

6A.10.1 Molecular Motions in Polymeric Solids Through Dynamic Mechanical Measurements, E. J. Tolle, Imass Company

6A.10.2 Modulus-Temperature Behaviour of Polymers by Means of the Automatic Measurement of the 10-Sec Relaxation Modulus as a Function of Temperature, R. Caspary, Dunlop, Germany

6A.10.3 A Dynamic Test Device for Vulcanized Rubber, W. G. Wanier, General Tire and Rubber Co.

6A.10.4 Use of a Supported Cantilever Vibration Mode for Determining the Elastic Constants and Viscous Modulus, C. D. Bopp, Oak Ridge, Tennessee

6A.10.5 Torsional Creep of Plastics, G. M. Armstrong, Tenessee Eastman Company

6A.10.6 Screening Test for Torsional (Shear) Creep of Plastics, Henry Gonzales, Jr., Tenessee Eastman Company

6A.10.7 Non-Linear Creep and Recovery on Viscoelastic Materials With a Cone and Plate Rheometer, G. L. Berry, Carnegie-Mellon University

6A.10.8 Molecular Relaxation in Amorphous Glassy Polymers by Thermomechanical Measurement of Thermal Shrinkage of Cold-Drawn Films, Hirotaro Kambe, University of Tokyo, Japan

6A.10.9 Nonlinear Viscoelasticity of Polymer Melts by Use of Large Amplitude Oscillatory Shear, J. M. Dealy, McGill University

6A.10.10 Uniaxial Extensional Viscosity of Polymer Melts, J. M. Dealy, McGill University

6A.10.11 Biaxial Extensional Viscosity of Polymer Melts, J. M. Dealy, McGill University

6A.10.12 A Rheometer for Measuring the Viscoelastic Response of Polymer Melts in Planar and Biaxial Extensional Deformations, Costel D. Denson, General Electric Company

Organic Polymer Characterization: Report
http://www.nap.edu/catalog.php?record_id=20350

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APPENDIX 6B

SELECTED POLYMER CHARACTERIZATION TECHNIQUES

Title

Embrittlement of Extrenally-Stressed Polymers in an Active Environment, 6A, 1. 9.

Purpose

Method of determining the load limits of polymeric materials in certain environments, below which there is no apparent change in physical properties.

Contributor

W. H. Haslett, Monsanto Company, Bloomfield, Connecticut

Primary Reference

W. H. Haslett, Jr. and L. A. Cohen, SPE, Journal, p. 246, March, 1964.

Equipment

A flexural holding device for maintaining a three point load on a suitable polymeric specimen. A special flex-fatigue fixture used with a universal testing machine (Instron, or equivalent), capable of cyclic crosshead motion between two deflection limits.

Sample Size

Ca 9.0 cm long, 1.27 cm wide and approximately 0.25 cm thick specimens cut from extruded or compression molded sheet. Specimens could also be injection molded.

Method

For a given material and environment a fail-stress in flexure vs. time-to-fail curve is generated. The surviving specimens are further exposed to flex-fatigue tests in air. By setting an arbitrary ductile/brittle point (survive or fail to survive a certain number of flexes at the same strains as in the static experiments) one establishes the ductile/brittle stress vs. time curve. From an engineering design standpoint this property is very important in setting the upper stress limit for a plastic part used in a given environment.

Limitations

The technique is valid for predicting performance only under conditions of the test for parts made by a particular process. Thus, testing of whole parts is superior to testing of standard size beam specimens.

Text References

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L. L. Lander, SPE Journal, 16, 1329 (1960).
J. V. Schmitz, and R. S. Hagen, SPE 17th ANTEC, Vol VII, paper 17-2, (Jan. 1961).
G. Salomon and F. van Bloomis, J. Appl. Polymer Sci., 7, 1117 (1963).
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General References

W. Weibull, Trans. Am. Sco. Mech. Engrs., J. Appl. Mech., 76, 293 (1951).
W. Weibull, Fatigue Testing and the Analysis of Results. Pergamon Press, New York, N. Y. (1961).
L. E. Nielsen, Mechanical Properties of Polymers, Reinhold Publ. Corp. 132, (1962).
A. M. Freudenthal, Handbuch der Physik, Band 6, Elastizität und Plastizität, 608 (1958).
N. E. Frost, Engineer, Vol. 200 (1955).

Committee Comments

This method should be broadly useful for parts subject to periodic stress in unusual environments, including those made of structural foams, adhesive-bonded composites and aircraft glazings.

Title

Dynamic Dielectric Analysis of Polymers, 6A. 2. 3.

Purpose

This technique is sensitive to changes in polymer molecular volume, weight, shape and electrical characteristics and therefore may be used in process control and materials science studies when investigating chemical kinetics, compatibility effects with plasticizers, configuration effects, degradation and stamina effects (and additionally free radical reactions and radiation curing methods), solubility parameters (through the Hildebrand solubility parameters concepts), adhesion (because forces between atoms and molecules are electrostatic in origin and are ultimately traceable to Coulomb's Laws of attraction and to dipole interactions: adhesive bonding forces, surface wetting and spreading, and diffusion); polymer morphology due to the relationship between crystalline structure and orientation with dielectric properties; thermal and thermomechanical properties; and in particular, relaxation properties which serve to interrelate mechanical, thermal and electrical responses.

Contributor

Stanley A. Yalof, President, Tetrahedron Associates, Inc.

Primary References

McCrum, Reed and Williams, Anelastic and Dielectric Effects in Polymeric Solids, Wiley, 1969; Hedvig, Dielectric Properties of Polymeric Materials, Adam Hilger, London, 1975.

Equipment

Dielectric spectrometers such as Tetrahedron's System 300 or System 400 with frequency ranges up to 1 MH_z.

Sample Size

Will accept liquids, powders, films, solids, typically one inch square and from 0.001 inches up to 0.1 inches thick, although almost any dimension can be accommodated.

Method

Materials are positioned between electrodes, which may be mounted within test cells or, in production circumstances within a forming tool, and by measurement of the interaction with an applied alternating electrical field we determine the dielectric relaxation behavior of a polymeric material throughout its cure.

Limitations

This is a relatively new field and much of the work has been directed toward solving problems of process control, rather than the determination of the relationship between dielectric and other relaxation responses. Also, many of the reactions studied are complex, involving irreversible and reversible effects due to thermoplastic behavior, chemical reactions, changes in polymer molecular weight and cross-linking. Thus, the sample which is being tested may be continuously changing with time, temperature and composition. Often it is not possible to isolate which of these changes is producing a particular dielectric effect, and in those instances it is necessary to cross-check dielectric methods vs. other techniques, and conversely.

References

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P. Hedvig and T. Czvikovsky, "Dielectric Spectroscopic Study of Wood Plastic Combinations", Ange. Makro. Chemie, 21, pp. 70-85 (1972).

Committee Comment

It is felt that this method should be useful for the characterization of thermosetting adhesives.

Title

Determination of Abrasion Resistance From the Time Dependence of Abrasion, 6A. 3. 11.

Purpose

Using this method, abrasion resistance of various specimens can be quantified and compared even when optical properties (opaque, transparent, different colors) as well as initial surface conditions (scratches) vary from specimen to specimen. It is the time dependence of abrasion which helps to eliminate these initial conditions. The method is especially suitable for evaluating consequences of abrasion on smooth (polished) surfaces.

Contributor

J. Bares, Xerox Corporation, Webster, New York

Primary Reference

J. Bares, J. Appl. Polymer Sci., 14, 1473-1475 (1970).

Equipment

Any oversimplified goniophotometer which determines angular distribution of light reflected from the evaluated surface. Suitable semiconductor photocell can be directly connected to a strip-chart or X-Y recorder. A setup for abrading flat specimens by carborundum powder.

Sample Size

Specimen (flat plate) with about 1 cm^2 of abraded surface. Sample size is usually determined by abrasion procedure.

Method

Surface abrasion and its progress with time is evaluated by comparing the intensity of light reflected by nondamaged parts of the surface (specular reflection) to that of light scattered by scratches (diffuse reflection). The specimen surface is illuminated by a narrow parallel beam of light and reflected light intensity is scanned over about 130°C in the plane of incidence of the primary beam. Recorded angular dependence of reflected light shows a sharp peak (specular reflection) and a broad peak (diffuse reflection). The ratio P(t) of peak surfaces, or even their heights, respectively, is further used. No absolute calibration is necessary since the unknown constants are eliminated using the time dependence of P(t).

Limitations

It is not clear how much of differences in optical properties and relative surface damage can be tolerated. Even in this method the comparison of optically similar materials with starting surfaces of approximately the same quality would give best results. Samples should be abraded by a random process. Abrasion intensity and times should be adjusted in such a way that P(t) does not reach extremely small (or large) values.

Text Reference

J. Bares, J. Appl. Polymer Sci., 14, 1473-1475 (1970).

General Reference

J. J. Gouza in Testing of Polymers, Vol. 2, J. V. Schmitz, Ed., Interscience, New York, 1966.

Committee Comment

This method should be useful in evaluating the abrasion resistance of materials used in aircraft glazings.

Title

Design Life Predictions Based on Combined Static and Dynamic Loading Strains, 6A. 3. 19.

Purpose

Eliminates the need for long term mechanical life tests on critical plastic parts by making use of a modified Goodman diagram analysis technique which incorporates the effects of dynamic and static loading strains.

Contributors

J. Nelson Knight, William R. Schlich and Donald T. Willian, General Electric Company, Schenectady, New York.

Primary Reference

J. N. Knight, W. R. Schlich, D. T. Willian, "A Novel Approach to Plastic Failure Analysis", SPE NATEC Preprint, p. 68, November 17-19, 1975.

Equipment

(a) Environmental Stress Cracking Tester - rectangular beam sample, simply supported, centrally loaded, constant load, sample in contact with the environment specific to the application. (b) Flexural Fatigue Tester - trapezoidal gage area, constant strain, mean strain equals zero, sample in contact with the environment specific to the application.

Sample Size

(a) Standard ASTM flex bars for ESCR test. (b) Fatigue sample size dependent upon type of tester used. Work to date has been conducted on test specimens prepared from extruded plastic sheet.

Method

(a) Actual strain measurements are determined on the plastic part in service utilizing strain gaging techniques. (b) Critical dynamics and static loading strains taken in the environment the part will be exposed to in service are determined in the laboratory. (c) A failure triangle is constructed by joining the critical dynamic strain (plotted on the ordinate) and the critical static strains in tension and compression (plotted on the abscissa). (d) Measured strains falling within the failure triangle should pass life test. Strains outside should fail.

Limitations

Universality of the technique has not been determined. The technique has been successfully correlated with a refrigerator inner door liner life test.

Text Reference

J. E. Shigley, Mechanical Engineering Design, McGraw-Hill, pp. 177-179 (1963).
R. J. Roark, Formulas For Stress and Strain, McGraw-Hill, pp. 39-41 (1965).

Reference

R. S. Hagen and J. R. Thomas, "Key Indicators for Plastics Performance In Consumer Products", Polymer Engineering and Science, 14, No. 3, March, 1974.

Committee Comment

This method may be useful for predicting the life of a wide variety of polymeric parts.

Title

Heterogeneities of Copolymers and Homopolymers by Thin Layer Chromatography, 6A. 4. 12.

Purpose

Qualitative and semiquantitative (relative) method of analysis and separation applicable to (1) analyze compositional heterogeneity of random and block copolymers (independent of their molecular weight distributions); (2) separate them by the difference in their chain architectures (e.g., alternating versus random copolymers, three-block versus two-block copolymers, and grafted versus ungrafted branch-chain and backbone-chain species in graft copolymer systems such as rubber-modified polystyrenes)--the method is also applicable to homopolymers; (3) for the determination of molecular weight distribution; (4) for the separation by the difference in stereochemical structures (such as iso- versus syndiotactic poly(methyl methacrylates), and cis-, trans-, and 1, 2-vinyl polybutadienes); and (5) for the separation by the difference in terminal groups (such as carboxyl group carrying low-molecular-weight polybutadienes from non-carrying ones). Many other applications would eventually be explored for the separation and semiquantitative analysis of synthetic polymers by very small structural differences.

Contributor

Tadao Kotaka, Kyoto University, Kyoto, Japan

Primary Reference

H. Inagaki, "Thin Layer Chromatography", in L. H. Tung (ed.), Fractionation of Synthetic Polymers, M. Dekker, New York, 1977 (in press).

Equipment

Any standard equipment[1] for low molecular weight compounds available commercially is sufficient for polymer work. Chromatoplates, usually 20 x 10 (or x 20) cm^2 glass plates coated with 0.25 mm thickness silica or alumina gel layer, can be prepared by the experimenters themselves, and also are commercially available. For quantitative purposes, use of a chromatoplate scanning device is advisable.

Sample Size

Depending on the sensitivity of detector available as well as on the properties of samples and other factors, sample size of as small as fractions of a microgram is enough. For ordinary purposes, the size must not exceed about 20 micrograms per one sample spot to avoid an overloading effect[2].

Method

The method is essentially the same as those for low-molecular weight compounds[1]. Samples are first spotted from stock solutions on a properly activated plate; then developed with an adequately chosen eluent system; and the relative flow rate R_f defined as the ratio of the migration rates of the sample to the eluent is determined for each sample (or discrete components, if any present, in the sample). If quantitative analysis is desired, the relative amount of each component as a function of R_f, thin layer chromatography-chromatogram, is to be determined by certain visualization technique[1-3], or by a scanning device[4], or by some other analytical methods. Although the thin layer chromatography separation is surprisingly sensitive to even very small differences in chain architectures, which are often indistinguishable by other analytical methods, and then is powerful in qualitative analysis, a quantitative interpretation of thin layer chromatography chromatograms, particularly of polymers, is usually quite difficult. The difficulty is partly due to inherent thin layer chromatography artifacts and partly to certain reasons specific to the particular polymer samples to be handled[1,3].

Text References

E. Stahl, *Thin-Layer Chromatography*, (M. R. F. Ashworth, translator) 2nd ed., Springer-Verlag, Berlin, 1969.

H. Inagaki, H. Matsuda, F. Kamiyama, Macromolecules, 1, 520 (1968).

T. Kotaka, J. L. White, ibid, 7, 106 (1974).

T. Kotaka, T. Uda, T. Tanaka, H. Inagaki, Makromol. Chem., 176, 1273 (1975).

General References

There is an extensive survey of the literature on the application of thin layer chromatography to polymer systems in the primary reference.

Committee Comment

It is felt that this method should be widely useful to characterize polymer materials or their precursors for significant changes in components present.

Title

Time-Temperature-Viscosity Characterization of Curing Thermoset Resins, 6A. 6. 2.

Purpose

This technique provides a means of approximating the viscosity-time behavior of thermosetting resins subjected to measurable time-temperature histories. Extensions and modifications of the technique are indicated. Correlation with actual processing conditions and resin response is indicated. Use in understanding and modifying existing quality control methods is presented[8].

Contributor

Mark B. Roller, Mobil Chemical Company Research and Development Laboratories, P. O. Box 240, Edison, New Jersey, 08817

Primary Reference

M. B. Roller, Polymer Engineering and Science, 15, 406 (1975)

Equipment

A cone and plate viscometer of sufficient resolution, range and stiffness to monitor the viscosity of small samples over the expected viscosity range, shear rates and temperatures. Systems should be clutched and easily cleaned of cured materials.

Sample Size

~20-30 mg as reported in primary reference. Can vary depending upon diameter and angle of cone and plate used.

Method

Determine the isothermal viscosity time behavior of material at several different temperatures. If possible correlate via Arrhenius type viscosity expression. Determine temperature dependence of isothermal parameters. Apply numerical integration technique to predict viscosity vs any heating profile. Set viscometer in dynamic heating mode and confirm model.

Limitations

Some materials do not follow simple Arrhenius behavior (see text Ref. 3) and more detailed analysis and modeling may be required coupling DSC and viscosity characterization. Some materials display adhesion problems as cure proceeds causing difficulty in determining isothermal curves. Some materials with volatile components or byproducts may be difficult to handle without applying external pressure. Some materials whose behavior during curing spans several orders of magnitude of viscosity in short times may require the piecing together of several experimental runs.

Text References

(1) M. B. Roller, Technical Papers, 33rd Annual Technical Conference, Society of Plastics Engineers, 212, Atlanta (May 1975).
(2) K. M. Hollands and I. L. Kalnin, Epoxy Resins, Adv. Chem. Ser. No. 92, 60, Am. Chm. Soc., Washington, D. C. (1970).
(3) M. R. Kamel, S. Sourour, and M. Ryan, Technical Papers, 31st Annual Technical Conference Society of Plastics Engineers, 187, Montreal (May 1973). M. R. Kamel, Polym. Eng. Sci., 14, 50 (1974).
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(5) S. D. Lipshitz, F. G. Mussatti and C. W. Macosko, Technical Papers, 33rd Annual Technical Conference, Society of Plastics Engineers, 239, Atlanta (May 1975).

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W. Aung, Proc. Internepcon Europa '73, Brussels, Belgium, 13 (1973).
W. Engelmaier, and M. B. Roller, Insulation Curcuits, 21, No 4, 43 (1975).
M. B. Roller, Technical Papers, 34th Annual Technical Conference, Society of Plastics Engineers, Atlantic City (April 1976) in press.

Committee Comment

This method should be useful for following the cure of thermosetting adhesives.

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APPENDIX 6C

MEASUREMENTS OF CHAIN SCISSION

Fracture is a complex phenomenon that despite considerable research is not well understood. The relatively complex morphology of polymers and the comparatively large strains that are generally associated with rupture in rubbers or plastics tend to make a mechanistic explanation of fracture in these materials particularly difficult. To gain better insight into failure mechanisms it would be helpful to have experimental observations that can be directly related to the atomic and/or molecular occurrences associated with fracture. Recently several investigations have made use of modern analytical instruments and methods to make such measurements. This work was pioneered by S. N. Zhurkov and his associates in Leningrad and has been extended in several other laboratories.

When homolytic scission takes place in a polymer chain, one might expect a pair of free radicals to be formed. Experimentally it has been observed that in some polymers and under proper conditions sufficient free radicals are produced (and these are sufficiently stable) for detection. One of the most sensitive means of detecting free radicals is Electron Spin Resonance Spectroscopy (ESR). Typical modern ESR spectrometers have a threshold sensitivity of about 10 free radicals in a resonant cavity ~1 cm in diameter by ~3 cm long[11]. ESR has been used to monitor free radical production and develop/check models and theories of failure in oriented polymers (fibers and films) in: (1) the USSR by Zhurkov and his associates[1-5]; (2) in the USA by Williams, DeVries, et al[6-9], by Peterlin, Crist, Verma and associates[10-12], and by Chaing, Davis and Sibilla[13-14]; (3) in Germany by Becht, Fischer and Kausch[15-18]; and (4) in Japan by Nagamura, Fukitani and Takayangi [19-20].

Andrews, Reed et al[21-23] as Queen Mary's College in London have used ESR to study low temperature fracture in prestrained rubbers. Related studies have been conducted by Brown et al[24-25] at the University of Utah, and Wilde[26] et al have extended the techniques to investigate dewetting-bond rupture phenomena in filled rubber systems.

Simonson[27-28] and his associates at the University of Utah have used ESR to study ozone-stress cracking in rubbers. They were able to demonstrate the validity of a "molecular scale" Griffith-type fracture mechanics analysis of ozone cracking.

An inherent difficulty in the use of ESR is that organic free radicals are generally unstable. After creation by chain scission the free radicals can react either with other free radicals or certain impurities and be annihilated in the process. This serves to limit the types of polymers, temperature, atmospheric conditions, time of testing, etc., that can be explored by this technique.

Recently Zhurkov and his associates[29-30] have reported on the use of infrared spectroscopy (IR) to measure the increase in end groups resulting from chain scission. This technique has the potential advantage that once end groups are formed they should be relatively stable. In principle this technique should result in an increase in the number of materials and testing conditions (e.g., higher temperatures, reactive atmospheres and long-term testing times such as creep and fatigue) amenable to study. While the reported general trends in behavior are similar in ESR and IR studies, there are significant differences in the numerical values of the number of free radicals and end groups as measured by ESR and IR, respectively. Additional studies are currently under way exploring the use of IR end group analysis of chain scission. In addition several groups[31-33] are investigating changes in molecular weight associated with deformation and fracture in polymers. While standard molecular weight determination techniques do not generally have the sensitivity of either IR or ESR, they do provide another standard for comparison as well as some information not available by these other methods.

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Organic Polymer Characterization: Report
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CHAPTER 7

PROBLEMS IN THE METHODOLOGY OF TESTING: THE CASE STUDY

INTRODUCTION

The characterization of polymers by means of tests might almost be a "hard" science, a branch of pure chemistry and physics, were it not that most characterization test goals involve prediction of performance in use. This forces, at some stage, a practical examination of (a) system utility together with composition of the material and (b) a factual record of experience in use of the material, prior and subsequent to laboratory examination. In most scientific systems, the ideal approach involves simplification of a problem, and reduction to the minimum number of factors which can be determined to be essential for an understanding of basic mechanism. The case study is often an admission that the current state of the science approaches that of an art, and that no simple adherence to fixed rules will necessarily allow close prediction of performance in all cases. So the case study usually must be wide ranging and consider failures as well as successes. An ideal case study structure is dependent upon the item, but in general one should consider all characteristics involved in both utility and failure. Once this is done, tests suggested can be considered first from the standpoint of their relevance to one or more aspects of utility and failure, and then the degree to which answers obtained can be unambiguous, even if not quantitative. Finally, but of equal importance, one must consider how closely the tests being examined apply to the item in its actual use system.

PURPOSES AND PROBLEMS

Case studies of the type presented consider techniques of testing at different levels. All are applied because they seem related either to superior or inferior performance in some describable instance. Mechanical as well as chemical tests are used in ways purporting to correlate with mechanical, physical, or even chemical action or reaction, but the correlation is often a complex function and not easily defined. High polymers are applied as prosthetics (skin, bone, blood or blood vessel substitutes) as well as machine structural members, supports, controls, windows, conduits, adhesives, and coatings.

Many accepted analytical and mechanical techniques that fill ASTM and similar standardization books may be useful pragmatically and applicable in case studies, but careful analysis of the facts of correlation are needed to show the degree of relevance. Many tests are no more correlated than time on a clock with the temperature outside; the result is that just when results of the test may be critical, incorrect answers are often obtained. Yet similar tests have proven of some value, if not too costly. One is a combination of the fact that they are done for lack of better, and have a long history behind them, so that major changes will at times indicate something novel has happened, which in turn will bring closer attention. This is important in laboratories where the testing personnel are frequently not knowledgeable, are bound by red tape or tradition, and not adequately informed as to the real requirements for the item in test. But too often, such tests are a cover for a lack of perspicacity and true interest, for carelessness, sloth, honest ignorance and effort to show effort despite a lack of understanding.

Many such tests are considered to be "finger prints". They identify Item B as identical to Item A. What is often forgotten in this case is that "finger prints" to be truly useful must be exact matches--not near matches. Moreover, the finger print identifies best with some past performance, and is less reliably a criterion of future action. The finger print is not a sine qua non of performance, since something else might be better, and a finger print, if not exact, may be totally misleading. Infra red spectrophotometry is often employed as a finger print, and this is not always advisable, since the sensitivity in charting and values for certain critical parts of high polymer molecules may be far too low, and reactive end groups may even be totally missed. Molecular structure alignments and characteristics are of extraordinary importance in affecting mechanical properties. For example, liquid crystal alignment has permitted spinning a fiber with more than double the tensile strength per unit of weight of any previous manmade organic fiber. This technology is still in its infancy, and undoubtedly will have reprecussions in other areas contiguous with the fiber field. The helical concept in polymer structure has long been recognized but spinning fibers into a helical structure is still ahead of us though cotton owes its remarkable bending resistance, despite its low stretch, to such inherent structure.

In special areas, such as Polaroid® polarizing sheets, quick set adhesives, pourable polymers, or semipermeable membranes, direct methods of characterization are observed by seeing if the product performs satisfactorily.

More complex is the problem of characterization for service life. Failure in use may have no direct relation with the characteristics which contribute to initial usefulness and failure tests, since they usually must be done in a time scale or under conditions far different from those involved in true performance, often proceed through mechanisms so different as to give misleading values. Oven aging tests, intended to correlate with performance at room temperature, are an outstanding example.

Hazard involvement characterization is another area of extreme complexity, where best practice needs constant review of what actually occurs. The plausible and the true often are not identical. At first view, the simplest failures seem to be fractures. In reality these are quite complex, since they can occur in organic polymers, as well as with metal and mineral structures, in many ways, including all of those known to occur in the older materials. In addition, sensitivity is found at much lower temperatures to creep, embrittlement, stress decay, aging effects and direction and rate of loading. Sensitivity to reagents which is not usually considered harmful, has been reported to affect aging and crazing of plastic windows. Unless mechanisms can be elucidated, improvement of properties and resistance to reagents depends on a trial and error approach. This is usually more time consuming and costly than if there were guidance through applicable theory.

Moreover, in hazard involvement, as with any other system in which human interaction occurs, to be forewarned is to be forearmed. Thus where corrosion of metals is anticipated, metal structures are given regular maintenance where permanent protection cannot be applied. Similar technology is needed for long service life in polymer applications. Flammability may be controlled by external approaches, e.g., monitoring of the use environment, use of sprinklers or restrictions on use of flames, cigarettes, matches, so that even a relatively flammable material, such as wood, can exist intact in complex structures for a long period.

A major function of the case study is to indicate what precautions will be needed and to negate a predictable failure mechanism. These precautions may involve standardized inspection and maintenance directives, involving overhauls, replacements and other renewals. On the other hand, in an item of which a polymer is a part the inherent limitations of the polymer may be transcended, e.g., as in a fail-safe using titanium straps to re-enforce adhesive bondings in aircraft.

NECESSARY CONSIDERATIONS

In any case study involving characterization, there are certain similarities. First, one must consider what is known about the product, its purity, and its constituents (the very important, less important, and those of little or unknown importance). The pejorative term "fillers" is often considered to denote a cheapening diluent or a way of reducing product costs. However, fillers often serve in polymer structures to add important qualities. This is clear from the addition of sulphur, zinc oxide or carbon black to rubber. Many cases are known where polymeric or non-polymeric materials are blended into the polymeric matrix to yield a product which is superior to the pure or "unfilled" material. These facts should be brought out in the average case study.

In dealing with a trade named product, if the product can be shown to have been previously satisfactory it is advisable to conduct tests which give some degree of assurance that today's product is not significantly different from yesterday's successful product.

Tests should concentrate on elements of known practical importance, even if these involve complex analyses of chemical materials or groupings not present in large percentages, e.g., active end groups, or catalytic trace elements. There are many simple, direct, and rapid tests, inter alia, pH, titrations, viscosity in solution, refractive index. These fast inexpensive tests may suffice in some instances; but, in no case should tests be done solely because they cost little. A rationale is needed for conducting each required test. Elemental analysis is often misleading, since elements may be present in different chemical and molecular forms. It is often the case, when commercial specifications have been made on the basis of quick and dirty fingerprint tests, that a technician can find ways to make a given material pass the specified tests without in any way demonstrating true performance characteristics.

If one knows how an item is supposed to perform and this performance is simple, the characterization task may also be simple. However, in general, performance is complex, and an analysis of reasons for failure, based, where possible on actual in depth failure analysis rather than on "logic" and "reason" is to be preferred. When not closely simulating actual operating conditions that may result in a failure one may be led far astray. Even some of the tests which purported to be similar to actual performance have been shown with the passage of time to be unrelated to the essential elements involved in true performance, often more complex than the so-called similar testing conditions allowed for.

Many polymer characteristics, determined by rapid approximate test methods, can readily be controlled and determined by a variety of compounding techniques so that while the appropriate values of these laboratory determinations may be useful, they cannot be considered sufficient for true characterization. Typical of such values are pH, viscosity, color, specific gravity, and others. Presence of spectroscopic absorption peaks may be controlled. Absence of such peaks is somewhat more difficult. Too complex a set of finger print tests can result in rejection of satisfactory material and could unnecessarily limit one's source of supply to the initial producer.

THE NEED FOR HANDBOOK TYPE DATA

Case studies expose the need for handbook type data. Generations of technical men as well as those with merely practical backgrounds, have compiled handbooks containing knowledge of when and with what to paint, how to galvanize, how thick this treatment need be for different real environments, how to recognize, identify and protect from corrosion, what are the usual limits of exposure and practical service life, etc. Such handbooks and background technology are still in their infancy in the polymer field. They are urgently needed if polymer products are to take a meaningful place in the design of bridges, buildings, boats, and other longer lasting vehicles and environmental structures.

On one hand, characterization should tell us whether a product is suitable for the purpose intended, if all other elements of usage are within previously considered bounds. On the other hand, characterization of the bounds of utilization may be, from a practical point of view, even more important, and if this characterization is not done, previously acceptable material may be found seriously at fault, especially as assurance based on past and cautious usage leads to growing demands on performance.

ANCILLARY CONSIDERATIONS

To be complete, case studies should take into account ancillary considerations. The case study for adhesives for example, notes the desirability of an etched metal surface. Possibly ultra-smooth planar or interlocking surfaces might be better, and determining the degree of etching may be of great importance. The case study should consider alternate solutions to problems, and even if these do not seem pressing, direction for improvement of future products should be suggested.

In a further example, structural foams effectively replaced wood and metal in many applications. Ease of formation into complex structures without machining, significantly lower density, and freedom from corrosion have foster applications. Questions of rigidity, thermal and sound insulation properties machineability, suitability of nails and screws in structure erection or degree of fire resistance all call for answers involving specific systems and environments. In the structural foam case study, somewhat general tables are presented for correlating properties important in utilization with the influencing factors both of product make up and use environment. While occasionally, applicable ranges are indicated, the numerical limiting envelope parameters and second or third order interaction effects are not given. So any new polymer applications such as carpet underlay, sound insulating ceiling or wall board, specific items of furniture, such as chairs, cribs, headboards, bicycle or automotive seat panel structures, still need more quantitative background information to be well designed. Handbook-type tables of property values are still to be developed and made readily available.

Case studies must indicate where current test methods fail to predict satisfactorily, as with consistent interfacial failures occuring in ways not duplicated by existing environmental durability tests with epoxy adhesives used for aircraft. Another example is glazing for aircraft, where the necessities for meeting both mechanical and optical specifications require entirely different test technology. Chemical and thermal interactions not yet fully understood may be involved. Goals for future improvement are thus set by pointing out existing shortcomings. If case studies do nothing else, they should direct one's attention to possible alternate solutions to existing problems. Even where suggested techniques are yet uneconomic or relatively unperfected, they should be mentioned. This type of information shows up well in the discussion of aircraft glazing. Attention is directed to specific areas where future work needs to be done, and where judicious funding could trigger significant desired improvements.

In every case study, the economic and actuarial aspect of characterization should be faced. A most unlikely cause for failure can hardly supply economic justification for testing to avoid it. One tests where there is significant potential for failure. Where characteristic can be safely taken for granted, or determined by little more than cursory examination, which may involve such elements as appearance, shipping weight, survival to the point of inspection, or immediate utility for an undemanding application, testing is uneconomic. Insisting upon it may encourage deceptions whose repercussions could involve those tests which in fact are justified. Test costs are essentially a form of insurance premium, in which every good item must pay a tribute to protect against the bad. The statistical aspects of this kind of testing have not always been looked at properly, since failures are not necessarily uniformly nor randomly distributed, and an average or random sample need not in fact be typical nor descriptive of the relatively few items out of control. The statistics of rare events and the concept of minimum life need investigation in many instances.

VIEW FROM THE TOP

The decision on what is adequate in testing is not entirely economic or rational, but may involve a sociological element. This may be a decision which needs regular review by managerial, not necessarily technical, experts, though the latter should be involved. Adequate testing, and its partner, societal impact, involve implications of both success and failure, not only of the product or type of product, but also of what went before and what happens after. Such problems involve very soft science, where experts frequently disagree, but for which consideration should be given at some stage. Technology assessment, potentials for future availabilities, price structures, by-product and waste disposal, test and maintenance costs, the cost to society, as opposed to initial costs to the individual user, may properly belong in a thorough case study, leading to a final valid set of recommendations not obtainable in a routine, narrowly aimed test approach.

CASE STUDIES

1. ADHESIVE BONDING: EPOXY ADHESIVES IN AIRFRAME CONSTRUCTION

INTRODUCTION

The purpose of this adhesive case study was to examine a situation where characterization of organic polymers has a significant role. It is an area where the recognition of characterization has recently evolved to a sophisticated state by pressure of need. This pressure to improve quality assurance has arisen from the airframe industry's desire to use adhesives in more significant roles in airframe construction.

Adhesives have been and continue to be used to advantage in the manufacture of airplanes. However, as use increased, certain manufacturing problems arose which indicated that the quality assurance for adhesives was lacking. These problems involved changes in curing response, handling characteristics, durability, and mechanical properties. Subsequent investigations were able to identify the causes of the departures from the norm, but one thing was clear in all cases, and that was the quality assurance was not adequate to preclude the problems.

The users of the materials called for better quality assurance than the suppliers wished to provide. Consequently, several aerospace manufacturers initiated research studies to answer their needs for improved quality assurance. Much material in this case study represents results of these efforts.

In preparing this case study, information on the manufacture of epoxy resins and their use in the airframe industry was obtained from three adhesive manufacturers, each of whom requested anonymity, and three representatives of the airframe industry, Boeing Commercial Airplane Company, Lockheed-Georgia Company, and McDonnell-Douglas Corporation. The areas of interest included: (1) Where are adhesives being used? What are the requirements for the particular application? (2) What adhesives are being used (by composition or suppliers and catalog identification)? (3) What tests do adhesive manufacturers perform to insure quality control? (4) What are the pre-established performance requirements? (5) What characterization is done by the airframe industry (chemical and physical)? (a) Acceptance criteria; (b) Shelf-life controls; and (c) Production line quality control of adhesive joint manufacture. (6) What additional methods of chemical or physical characterization are needed?

The adhesive manufacturers were reluctant to provide detailed information for a number of reasons. The proprietory adhesive formulations are considered non-patentable. The manufacturers' position is that disclosure of adhesive composition will result in the production of adhesives by low-overhead competitors. Because of this, the manufacturers were unwilling to disclose the formulas of their compounds, even those more than three years old and no longer used. Furthermore, since the manufacturers felt that revealing the quality assurance tests and controls they require would divulge the composition of their products to their competitors, this information was not made available to the subcommittee.

Usually, the adhesive manufacturer will not give proprietary information to the customer, but will agree on the critical parameters with the buyer, including the test schedule and test frequency. Certain manufacturers have changed their policies recently and will enter into confidentiality agreements with the aerospace industry, providing information as to the chemical identity and testing.

Because of the competition in adhesive manufacturing and the ease with which a small manufacturer can enter the business, the supplier usually sets his own tests and defines the limits. Since testing is a large portion of the cost of the adhesive, the larger suppliers take the position that they are selling reliability.

ADHESIVE BONDING IN AIRFRAMES - AN OVERVIEW

The adhesive bonding in the production of the Lockheed L-1011 Tristar and the repair of fatigue cracks at a wing joint of the Lockheed C-5 aircraft are outlined in this section to provide a perspective of requirements and problems in the airframe industry. There are other commercial and military aircraft which employ adhesive bonding in airframe construction. The Air Force F-111 and F-15 and the Navy F-4 Fighter-interceptor and the F-14 carrier-based fighter are a few examples.

DESIGN AND MANUFACTURE OF THE LOCKHEED L-1011 TRISTAR

THE PROBLEM

The problem of wide-body aircraft design and manufacture centerd on the production of an airplane durable enough to give unlimited structural life in normal service. Increased fatigue life and trouble-free service could presumedly be obtained through adhesive bonding. Initially the unknowns were: (1) Could an adhesive bond provide sufficient strength? (2) Would a total adhesive system resist corrosion? (3) Could an adhesive bonding production afford top quality airframes?

The adhesive bonding concept had the advantages of providing lighter weight panels, more fatigue resistance and better aerodynamic smoothness, but the solution to the problem in providing an airframe with unlimited life depended on the ability to inhibit corrosion. Moisture induced failure was further aggravated by the fact that the bonded structures are difficult and expensive to repair.

INITIAL TESTING

The fatigue test article is expected to have completed cycle loading equivalent to 20,000 flights. Although metal bonding did not replace mechanical fastening on the Tristar, it eliminated 200,000 rivets and fasteners on the airframe and produced an increased fatigue resistance. The test program identified the following advantages: (1) Uniform Load Distribution (as opposed to local fasteners); (2) Resistance to Crack Propagation (crack growth retarded on arrival at a bondline); (3) Fail Safe Improvement (bonded titanium straps); (4) Sonic Fatigue (bonded structures show a self-damping characteristic); (5) Acoustical Absorption; (6) Lighter Structures; and (7) Minimum Maintenance.

DESIGN AND PRODUCIBILITY

The Tristar body is a conventional semimonocoque shell with a constant cross section of 235-inch diameter along most of the length. Bonding is utilized throughout the 150 feet of airframe pressurized zone to join doublers and triplers around openings in the skin. Skin and stringers are supported by sheet metal frames at 20-inch intervals. The size of the skin panel assemblies can range in size up to 38 feet by 15 feet (Figure 1).

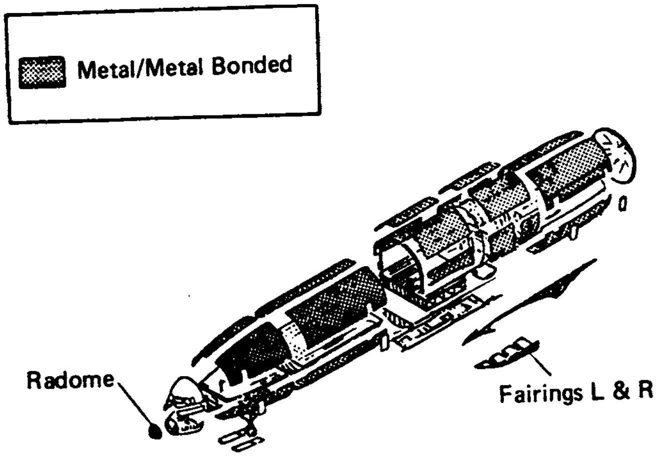


Figure 1. Structural Bonding-Fuselage

Bonded primary structures include fuselage skin panels, fail safe straps, floors, longerons, plank tab ends and pads, bulkheads (pressure fuel, and underfloor), and pylon panels. Bonded secondary structures are ailerons, flaps, spoilers, fairings, surface panels (wings and tail excluding box area), leading edges, and slats.

The construction required an adhesive with high shear strength, high peel strength, bond line resistance to corrosion, minimum degradation of properties due to adverse environments such as extreme temperatures and corrosive liquids, and not requiring a cure temperature above 260°F. Room temperature curing adhesives were available but they were not as strong and did not have a high enough heat distortion temperature. Other criteria for adhesive were: (1) Uniform strength reproducibility; (2) Proven service of the Adhesive Chemical Class; (3) Non-wicking carrier; (4) Corrosion inhibiting primer; and (5) Repairability in service.

MANUFACTURING AND PROCESS CONTROL

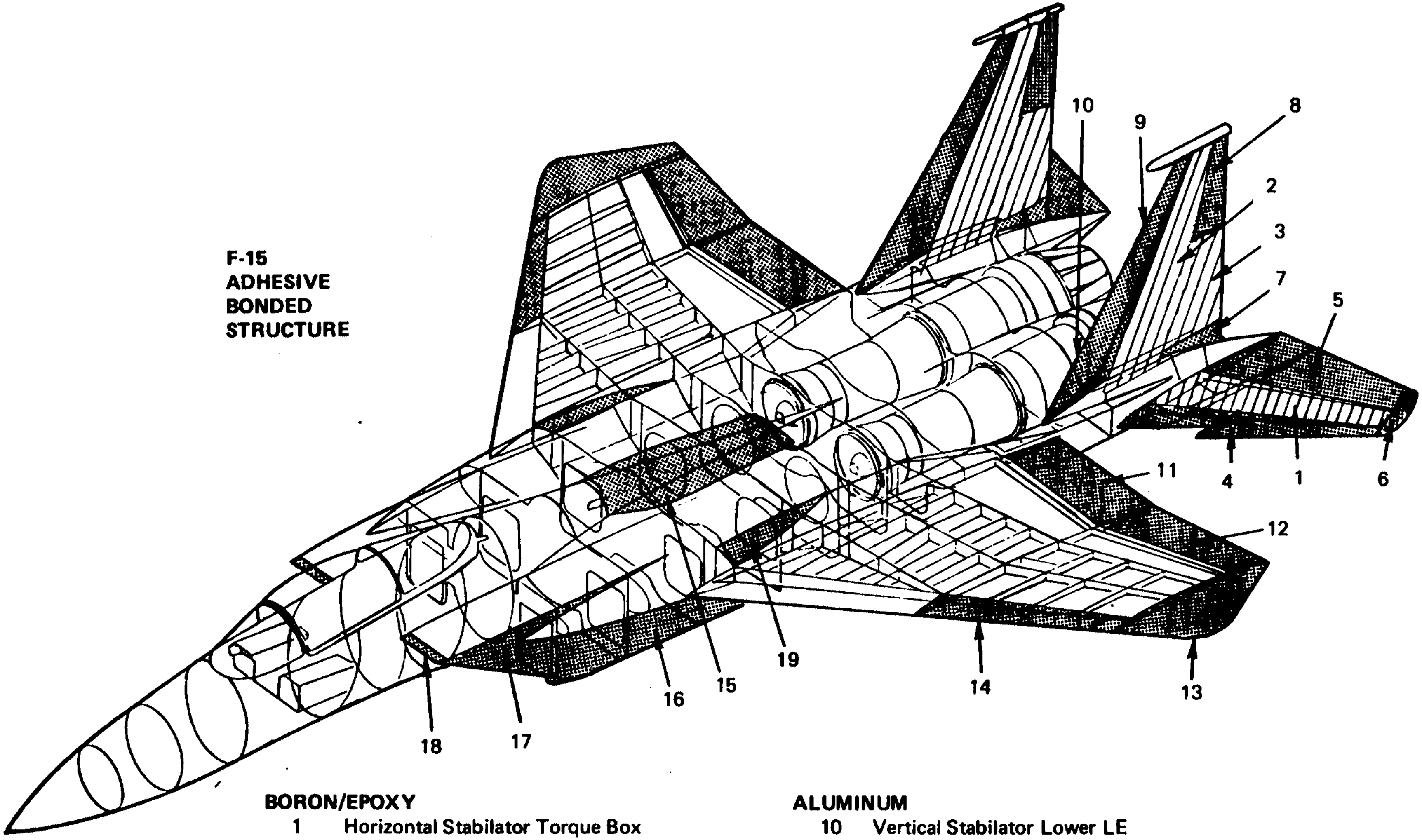
The bonding complex for the Tristar consists of eight major processing points connected by 5 1/2 miles of overhead conveyor system. (1) The skins are sprayed with an elastomeric protective coating. (2) The stretch press shapes the panels to tolerances as close as 0.015 inch. The roll bends panels of constant curvature. The protective coating is not affected by either of these machines. (3) At the pre-fit line, panels are installed in metal bond fixtures for pre-fit of doublers, triplers, fail-safe straps, etc. (4) In the cleaning line, the panels, doublers and straps pass through an alkaline wash, rince and drying to remove the protective coating. (5) The metal surfaces are etched with a dichromate bath to provide a surface for maximum adhesion. The surfaces are rinsed thoroughly and dried. (6) An adhesive primer (Br-127 epoxy) is applied in a uniform coat (0.1-0.2 mi) by spraying, heating to flash off the solvent and then curing at 250° for one hour. Process control is obtained at this point by obtaining peel strengths at -67°F. (7) Primed panels are held in a "clean" room until called to the layup room where the adhesives are applied to the panel and the layup is completed. Strict contamination control is exercised in the layup room. The adhesive (FM-137 epoxy) is applied in a solvent containing 12-15 percent solids and a Dacron® cloth carrier in thicknesses at 0.010 in. during layup, flowing to 0.004 and 0.007 in. during cure. The panels are shrouded in plastic bags and a vacuum is introduced inside the bag to a pressure of about 10 psi creating a downward pressure on the part. (8) The panels inside the bag are cured in an autoclave at 250°F under 135 psi. This is accomplished by sealing the autoclave and pressuring with an inert gas to 110-115 psi, during which the vacuum to the sealed bags is shut down and the hoses are vented to the atmosphere. The pressure is then raised to the final 135 psi and the temperature is raised to 250°F. The total cure time is 3 1/2 hrs; the final temperature and pressure is held for 1 hour followed by 1 hour for cool down.

The first step in inspection is test of the peel (climbing drum peel ASTM D1781-62) and lap shear (ASTM D1002-72) coupons which accompany the panels through production. Ultrasonic inspection of the panels for voids was performed manually initially; automated scanners are presently in use.

The painting and bond line covering sequences are further provided for elimination of corrosion.

The panels are made into quarter-section subassemblies, then into half sections, and finally into full barrel segments followed by mating the segments into the complete pressure vessel.

As mentioned earlier, aircraft in service have employed adhesive bonding in various structural parts. Figure 2 shows the areas in the F-15 employing adhesive bonding.



F-15
ADHESIVE
BONDED
STRUCTURE

BORON/EPOXY

1	Horizontal Stabilator Torque Box
2	Vertical Stabilator Torque Box
3	Rudder Torque Box

ALUMINUM

4	Horizontal Stabilator LE
5	Horizontal Stabilator TE
6	Horizontal Stabilator Tip
7	Rudder Fairing
8	Vertical Stabilator Upper TE
9	Vertical Stabilator Upper LE

ALUMINUM

10	Vertical Stabilator Lower LE
11	Landing Flap
12	Aileron
13	Wing Tip
14	Outer Wing Leading Edge
15	Speed Brake
16	Inlet Nacelle Outboard TE Side Panel
17	Variable Intake Panel
18	Inlet Nacelle Upper LE

POLYESTER PREPREG

19	Wing Fairing

Figure 2

The Boeing Company also uses adhesives in metal to metal bonding and metal to honeycomb bonding. Metal to metal applications include such structural items as tear straps, doublers, triplers, etc. Honeycomb bonding is presently restricted to secondary structures such as spoilers, ailerons and flaps. In Boeing's YC-14, however, metal/honeycomb structure is employed in the inspar skins of the horizontal and vertical stabilizer. Metal/honeycomb bonding has received wide usage in structures designed for acoustic attenuation.

REPAIR OF THE C-5 TRANSPORT

A major consideration in airframe adhesive bonding is the ease and cost of repair. This problem arose in the C-5 when fatigue cracks developed at a wing joint. Repair was effected by bonding thick doublers (0.45 in) to the top and lower surfaces of the wing.

PRELIMINARY TESTING

Preliminary considerations included adhesive testing, producibility, fastner selection and a full scale layup. It was recognized that there would be a variation in bond line thickness because of the thickness of the doubler, and that this would affect the shear strength. The adhesive qualification included a consideration of the cure temperature and the fact that the surface already on the aircraft would have to be removed by hand. Fatigue testing results on three riser components showed 116,000 cyclic test hours on the baseline configuration and 180,000 cyclic test hours on the bonded doubler. There was good correlation between the components and the full scale test articles.

SEQUENCE OF REPAIR

(1) A prefit and drilling. (2) Verification of the bond cycle. (3) Cleaning of the wing and doubler. This sequence included hand removal of the paint, a rinse, an Alconox scrub, a surface treatment and a corrosion inhibiting primer. (4) Application of the adhesive (3-M, AF 127-3). (5) Bonding. (a) Application of pressure on the doublers by bolting and application of torque. Later a fluid press with a mechanical bladder was used. (b) Applying a heater blanket and curing at 215°F. Automatic temperature control was maintained with a series of thermocouples because of the heat sink differences in different areas of the doublers. These thermocouples in turn controlled individual heaters. (6) Inspection (ultrasonic).

EPOXY ADHESIVES: COMPOSITION AND CHEMISTRY

A variety of different epoxy adhesives is currently being used by Boeing, Lockheed and McDonnell-Douglas in aircraft. Little or no information is made available to the airframe industry by the adhesive manufacturers concerning composition and structure of the materials or chemical reactions involved.

CURRENT SYSTEMS

The list of 250°F and 350°F cure adhesives and primers supplied to Lockheed is given in Table 1. The 250°F cure adhesives are used in subsonic aircraft. In addition, a 250°F curing AF 55 newer generation adhesive system is undergoing tests. The suppliers of these systems were not identified.

The adhesives used by McDonnell-Douglas in the various aircraft are listed in Table 2.

Boeing has used primarily adhesives produced by American Cyanamid, FM 123, and 3M, AF 126. With the introduction of Boeing's new specifications covering advanced structural adhesives, the supplier list has been expanded to include Hysol and Goodrich. All are 250°F curing systems with nearly the same engineering properties but with wide differences in composition. Composition is not stipulated in specifications, but it is established and controlled in an agreement between Boeing and each supplier.

With the introduction of the "Advanced 250°F Curing Structural Adhesives" specification, Boeing has initiated an attempt stipulating chemical compositional control including analytical techniques mutually agreed upon with the supplier. This includes an agreement to preserve the supplier's proprietary interest and represents a first step in obtaining a chemical knowledge of the adhesive.

250° Cure		350°F Cure	
Adhesive	Primer	Adhesive	Primer
AF 127-3	EC 3921, EC 3926	AF 31	EC 2174
Plastilock 717	720, 721	FM 61	BR 227
EA9601	EA 920, EA 9209.1	FM 96	BR 227A
Reliabond 393-1	Type 5, Type 7	FM 1000, EP-15	BR 1009-(8, 49)
FM 123-4	BR 125, BR 123	HT 424	HT 424
FM 123-2	BR 125, BR 123	Metlbond 328	Metlbond 328
FM 137	BR 127	Reliabond 398	Reliabond 398
		Metlbond 329	
		AF 143	EC 3917
		Plastilock 729	Plastilock 728

Table 1

ADHESIVES USED BY MC DONNELL-DOUGLAS

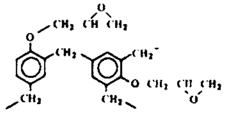
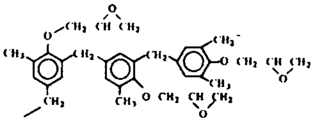
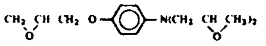
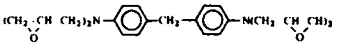
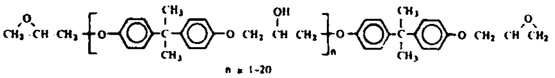
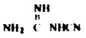
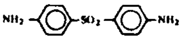
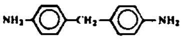
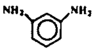
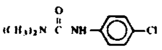
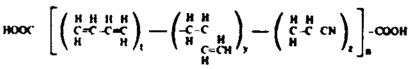
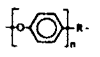
AIRCRAFT	PRIMARY ADHESIVE SYSTEM	CURE TEMP. °F	SUPPLIER	SERVICE TEMP°F	STRUCTURES
F-15	FM-400 Supported film (epoxy) FM-404 Foaming film (epoxy) BR-400 Primer, Corrosion inhibiting	350	Am. Cyanamid	-65 to 420	Aluminum and composite honeycomb sandwich
F-4	FM-96 Supported film (epoxy) FM-61 Supported film (epoxy/nitrile phenolic) BR-227A Primer (epoxy)	350	Am. Cyanamid	-65 to 350	Aluminum honeycomb
DC-10	FM-123-2, Supported film BR-127, Primer	250	Am. Cyanamid	-65 to 180	Metal to Metal only finger doubler for sonic fatigue resistance
	EA-9602 Supported film		Hysol-Dexter		
	AF-151 Supported film EC-3924 Primer		3M		
	AF-32 Unsupported film (nitrile phenolic) AF-202 Supported film (epoxy/nitrile epoxy) EC-1660 Primer	300	3M	-65 to 180	Aluminum honeycomb sandwich
	EA-951 Unsupported and supported film (Nylon Epoxy)	350	Hysol-Dexter	-65 to 200	Aluminum honeycomb sandwich
	FM-1015 Unsupported and supported film (Nylon Epoxy)		Am. Cyanamid		

Table 2

COMPOSITION

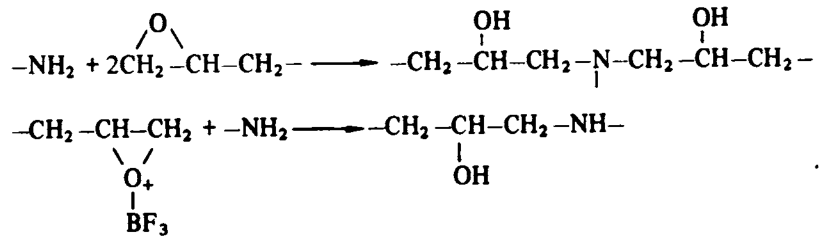
Epoxy adhesives are formulated from different classes of components: the epoxy curing agent, catalyst, flexiblizer and filler. Which compound or combination of compounds in each class is presented in the formulation depends on the performance requirements for the adhesives. Some representative compounds in each class are listed in Table 3.

TABLE 3 Epoxy Formulations

Class	Name/Origin	Structure
Epoxy	Polyglycidyl ether of Phenolformaldehyde Novolac Example: DEN 431, DEN 438	 (a representative structure)
	Polyglycidyl ether of *o*-Cresolformaldehyde Novolac Example: ECN 1299	
	Triglycidyl *p*-Aminophenol Example: ERL 0510	
	Tetraglycidyl-4,4′-diaminodiphenylmethane Example: MY 720	
	Diglycidyl ether of bisphenol A-epichlorohydrin reaction Example: EPON 828	
Curing Agents	Dicyandiamide (DICY)	 $NH_2\overset{NH}{\overset{\|}{C}}NHCN$
	Diaminodiphenyl sulfone (DADPS)	
	4,4′-Methylene Dianiline (MDA)	
	m-phenylenediamine (MPDA)	
Catalysts	Boron Fluoride Amine Complex (Also a curing agent)	$CH_3CH_2NH_2 \cdot BF_3$
	Triphenylphosphine	$(C_6H_5)_3P$
	N,N-Dimethyl-N′-(4-chlorophenyl)urea	
Flexibilizers	Hycar Nitrile Rubbers (carboxyl capped butadiene-acrylonitrile copolymer)	
	Phenoxy resins	
Fillers	Silica	$(SiO_2)_n$
	Silicates (e.g., asbestos)	$(MgSiO_3)_n$
	Metal Powder	Al

CHEMISTRY OF CURING

The basic reactions are those involving nucleophilic attack of the amine on the epoxide function, which affords a three-dimensional network structure. Where the amine is poor nucleophile (e.g., DDS) a boron fluoride amine complex is added to assist the opening, or in the case of DICY, the urea derivature is added. DICY is a "latent" curing agent by virtue of its insolubility.



$$-NH_2 + 2\,\overset{O}{\overbrace{CH_2-CH}}-CH_2- \longrightarrow -CH_2-\overset{OH}{\overset{|}{C}H}-CH_2-\underset{|}{N}-CH_2-\overset{OH}{\overset{|}{C}H}-CH_2-$$

$$-CH_2-\underset{\underset{BF_3}{\overset{|}{O^+}}}{\underbrace{CH-CH_2}} + -NH_2 \longrightarrow -CH_2-\underset{OH}{\underset{|}{C}H}-CH_2-NH-$$

In addition, the reaction of a carboxyl group with an epoxide (in the presence of a triphenylphosphine) can form a linear ester.

$$-CO_2H + \overset{O}{\overbrace{CH_2-CH}}-CH_2- \longrightarrow -\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{OH}{\overset{|}{C}H}-CH_2-$$

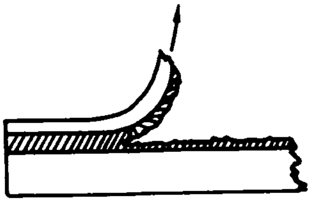
Fillers are added to: (1) Control the viscosity. (2) Reduce thermal coefficient of expansion in the cured resin. (3) Minimize shrinkage during curing. (4) Improve resistance to elevated temperatures. (5) Lower cost.

MECHANICAL TESTING METHODS: A DESCRIPTION

Three different modes of stressing an adhesive joint to bring about failure are shear, tension, and cleavage:

Lap Shear

Tension



Peel

The first two correspond to forces acting on rigid adherends while the last corresponds to tensile loads transmitted to the interface by a flexible adherend.

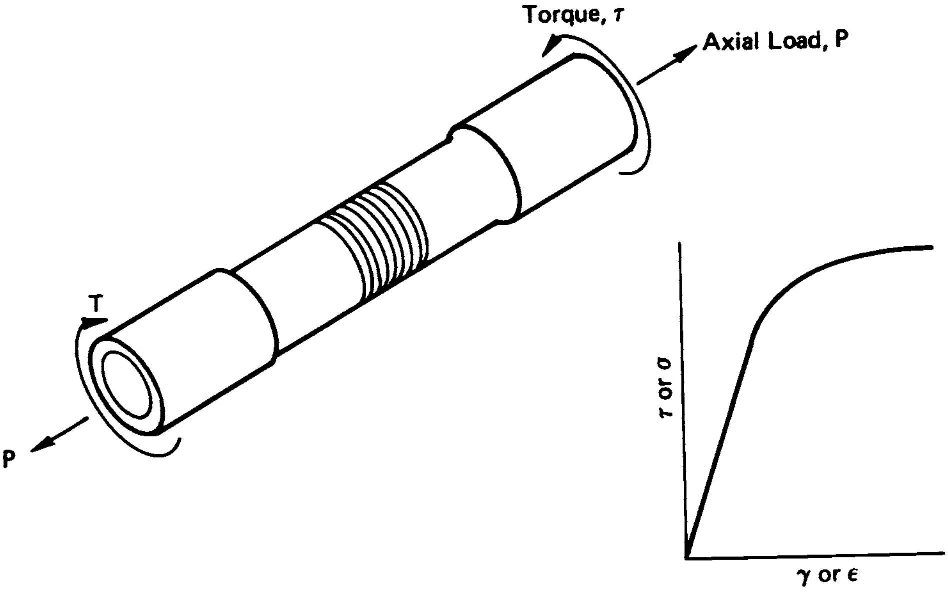
Three different mechanical tests are used with adhesives, lap shear, torsional ring, and peel strength, all of which are destructive tests. The most common and desirable mode of loading the joint is in shear.

LAP-SHEAR

The tensile lap-shear test of an adhesive is used almost universally. The method has the advantage that specimens are easy to fabricate, and they lend themselves to economical testing at various temperatures or after aging at various temperatures. There are problems with this method of testing, however. Because the bonding adhesives are usually very thin, the stress distribution is not uniform. Data obtained from the standard lap-shear tests (ASTM D1002-72) are questionable for design purposes.

TORSIONAL-RING OR "NAPKIN RING"

In principle a shear test is better if a bonded joint is subjected to torsion. The "napkin ring test" (ASTM E229-70), which has rod or tublar adherends bonded together, has the advantage that if the annular width is small compared to the diameter, the shear is uniform over the entire joint (Figure 3). The disadvantages are that the ring specimens are difficult to fabricate accurately and reproducibly, and curing of the specimen at elevated temperatures may result in somewhat different film properties than in a lap joint between adherends.



Typical Test Result

Figure 3

PEEL TEST

Although peel strength is not usually a design criterion, the manufacturer is interested in achieving high peel strength; the designer recognizes the damping characteristics associated with high peel strength and the resultant impact and fatigue resistance. It is an easily measured process control property. Good peel strength is specified from the adhesive formulator.

The climbing drum peel (ASTM D1781-62), T-peel (ASTM D1876-72) and Bell peel tests are not used as extensively as lap-shear, although peel strengths are published for many adhesives. Although the test is useful in comparing toughness of adhesives, changes are induced by varying temperatures, testing speeds, surface cleaning treatments, etc.; its values are not directly usable by design engineers.

CHARACTERIZATION AND QUALITY CONTROL BY SUPPLIER

Because of the refusal of the adhesive manufacturers to provide direct information on composition, testing, and quality control of the adhesives, two hypothetical adhesives were proposed, a 250°F curing resin and a 350°F curing resin. The following information is a composite summary of the methods for the characterization and control of performance of the hypothetical adhesives that were reported by the manufacturers as being useful.

The two hypothetical formulations presented were:

250°F Curing Resin:

	Parts	Material
Prereacted	50	DEN 438, an epoxy Novolac
	50	EPON 828, a bisphenol A epoxy
	10	CTBN, a carboxyl terminated acrylonitrile-butadiene copolymer
	1	Triphenylphosphine
	6	DICY, dicyandiamide
	5	1472, a higher molecular weight/acrylonitrile-butadiene copolymer
	4	N, N-dimethyl-N'-(4-chlorophenyl) urea
	35	Asbestos
		Nylon Cloth Carrier

350°F Curing Resin

	Parts	Material
Precooked to Solubilize DDS	90	MY 720 Tetraglycidylmethylenedianiline
	10	DEN 438, an epoxy Novolac
	50	DDS, Diaminodiphenylsulfone
	150	Aluminum Powder
	1.5	Boron fluoride ethylamine complex
		Fiberglass Cloth Carrier

In both hypothetical systems some prereaction would be present, such that it would not always be practical to fractionate the components or even to analyze individual components and reaction products. The following are methods which can be used for characterization. It should be noted that controls on incoming raw materials may also be imposed.

INFRARED

This is the simplest, most versatile, and widely used analytical technique available. Spectra are obtained by trained personnel on high-quality instruments and interpreted by those knowledgable in infrared spectroscopy. Epoxide content (910-195 cm^{-1}) and nitrile rubber content (970 cm^{-1}) can be compared with an internal standard (shoulder on aromatic peak at 815 cm^{-1}). Dicyandiamide and nitrile content could also be obtained by infrared. The sulfone band (1105 cm^{-1}) could be used to calculate diaminodiphenyl sulfone content. Thus, the spectrum would be characteristic of the epoxy system but the identity of the resins and their ratio could not be determined. For example, HYCARS CTBN and 1472 could not be differentiated.

The 350°F prereacted curing resin could be insoluble and therefore dissolving the organic portion away from the filler and carrier to obtain transmission infrared would not be feasible. The ATR spectrum could be obtained, however.

GEL PERMEATION CHROMATOGRAPHY

This procedure can be very useful, but involves considerable time and effort. Usually this method is not warranted unless special problems develop. In general, the soluble portion of the system can be analyzed as to the molecular weight distribution; high and low molecular weight portions can be identified as an indication of the extent of the reaction. This analysis is appropriate for the epoxy and the nitrile rubber polymers.

EPOXIDE EQUIVALENT WEIGHT

A fast method for chemical epoxide content as an alternative to an infrared determination.

ELEMENTAL ANALYSIS

Useful for obtaining total sulfur, fluorine and nitrogen, particularly in the 350°F curing system.

DIFFERENTIAL SCANNING CALORIMETRY OR DIFFERENTIAL THERMAL ANALYSIS

This method will give the temperature of initiation of curing (exotherm) and may indicate the quantity of catalyst and/or curing agent as well as the extent of advancement of the reaction.

MISCELLANEOUS

The fillers can be determined by ashing the film. The carriers (nylon or glass fiber) can be washed free of resin and examined for weave. In the case of the nylon carrier, the type of nylon can be identified by infrared spectroscopy.

The gel time of the adhesive can also be measured. The flow of the adhesive during fabrication is critical to its performance. Flow out of the bond line during cure under pressure can be compared to a standard curve (Audry Cure Curve).

One of the most difficult problems for the supplier of an adhesive is the great diversity of process procedures employed by the different users. Ultimately, performance testing over a temperature range provides the acceptance criterion for both the resin and the fabrication procedure. Fracture toughness (-67° to 250°F or 400°F), wide area overlap shear (-67° to 250°F or 400°F), and peel tests (75°F)--such as bell peel and honeycomb peel--can be carried out on samples.

An individual manufacturer may not employ all these characterization methods, since some of the methods afford an overlap of information and there are individual preferences in the method. The kind and extent of testing will also vary with the adhesive end use.

CHEMICAL AND PHYSICAL CHARACTERIZATION BY THE AIRFRAME INDUSTRY

Performance requirements, acceptance criteria, shelf life controls, and production line quality control of adhesive joints with each company are similar, as far as could be determined. Specifications for adhesives rely upon defining a series of performance parameters and do not consider the characteristic of the polymer which provides this performance.

PERFORMANCE REQUIREMENTS

Boeing performance requirements include all that are stipulated in relevant government specifications such as shear, peel, and interfacial tension at low, ambient, and elevated temperatures and after environmental exposure. Additional Boeing requirements stipulated are sustained load and fracture propagation. These performance requirements relate to as-received material and to material after aging for 15 days at 90°F.

Lockheed performance requirements which were outlined include Military Specifications that do not address the problem of composition (MMM-A-132, MIL-C-7438F, MIL-A-25463A, MIL-A-83376 and MIL-A-83377). Although lap-shear is considered inadequate; metal-to-metal requirements persently include this test (L/t of 8, 24 and 40) at -67°F, room temperature and upper service temperature. Lap-shear is specified after the specimen has been subjected to cyclic environmental salt spray and fluid immersion. Peel strength (-67°F, room temperature and upper service temperature) and creep rupture/deformation (room temperature and upper service temperature) are also performance requirements.

Metal to core requirements include flatwise tensile, flexure shear, and climbing drum peel; all at three temperatures.

McDonnell-Douglas provided the performance requirements for the various aircraft and adhesives shown in Table 4.

AIRCRAFT	ADHESIVE	TEST/REQUIREMENT
F-15	FM-400	Shear at room temperature, 365°F and 420°F.
	BR-400	Climbing Drum Peel, room temperature.
	FM-404	Honeycomb Beam Shear, room temperature.
		Aging tests should meet requirements of MMS 307 after aging for 90 days at 40°F, 60% RH or less or 5 days at 90 ± 10°F.
F-4	FM-96	Shear, room temperature and 350°F.
	FM-61	Climbing Drum Peel, room temperature.
DC-10	DMS-1911	Shear
	DMS-1633	T-Peel
	DMS-2103	C/D Peel

Table 4

An example of performance requirements of McDonnell-Douglas adhesives is given in Appendix A. These include storage temperature, shelf life, primer curing conditions, and lap shear requirements for bonded specimens.

ACCEPTANCE CRITERIA

Rigorous acceptance criteria, especially with regard to chemical and molecular composition are lacking. Lap-shear tests are carried out by all three airframe companies. Acceptance testing can include any or all of the performance tests plus those necessary to insure manufacturing suitability. McDonnell-Douglas includes thickness and weight requirements. Boeing performs compositional analysis as a receiving inspection, but this is not done on every batch. A sampling procedure is carried out and non-conformance is grounds for rejection.

SHELF-LIFE CONTROLS

Shelf life is characteristically specified in performance requirements (see for example, Appendix A), but it was not apparent that a routine inspection or testing of shelf samples was carried out. The deletion of unacceptable shelf material would evidently be revealed in the production line quality control.

PRODUCTION LINE QUALITY CONTROL

Production line quality control for the three manufacturers includes test specimen monitoring of surface preparation, primer thickness control, adhesive layup and tool qualification and ultrasonic or destructive examination.

Lockheed quality control begins with lap-shear and peel strength tests on received samples. Inspection of holding tanks and lines and destructive tests on tag specimens are routinely performed. The scanning electron microscope is being used to look at the surface of failed structures. Visual ultrasonic and X-ray inspection are nondestructive inspections performed on the panels.

Testing the fatigue life of an airplane or testing after the airplane has been in service presents serious problems in that usually nondestructive tests must be employed. Approaches to this problem include destructive testing of plug samples and in-service acoustic emission monitors.

Although it is evident that Lockheed is employing modern techniques in control such as DSC, gel permeation chromatography, chemical, analysis, infrared spectroscopy, thermomechanical analysis, thermogravimetric analysis, microscopy, and dynamic and dielectric analysis at various stages of manufacture, the details of how and where these analyses were applied were not covered.

The stipulation of chemical composition control analytical techniques which has been agreed upon between Boeing and the suppliers was not provided.

A more comprehensive review of the proposed analytical procedure to be carried out by McDonnell-Douglas represents a fundamental approach to adhesive quality control. Overall control includes incoming inspection, reinspection after set shelf life, storage (log kept on each batch), controlled cure, process control tests with each assembly, and the nondestructive radiograph and ultrasonic tests.

The instrumental resin control scheme is given in Figure 4 and the resin system and the analytical techniques are outlined in Figure 5. Separation of the resin is accomplished by gel permeation chromatography (Appendix B), and identification is accomplished primarily through infrared spectroscopy using computer search and match up procedures (Appendix C). Analytical characterization is carried out by differential scanning calorimetry (Appendix D).

Ongoing research at Boeing[1], Lockheed[2], and McDonnell-Douglas[3] is aimed at insuring reliability in the test methods and the development of new methods to improve quality assurance.

CONCLUSIONS AND RECOMMENDATIONS

Important conclusions concerning problems and needs in adhesive bonding are apparent. There is a need for improved quality control, greater design confidence (designers are conservative, and tend to overdesign), and a basis for service evaluation (time to obtain information from aircraft in service is long). Moisture is the chief enemy in structural bonding, and the difficulties which arise because of this need to be overcome. The most critical processes in adhesive bonding are surface preparation, intimate contact, and adhesive cure. Probably the single most important factor in producing reliable environmentally stable bonds is the surface preparation. From this study the following problem areas have been identified: (1) There is little quality assurance at the user level. (2) The users generally know neither the formulation nor the chemical test methods used by the suppliers for quality control. (3) The adhesive manufacturer is reluctant to cooperate in the disclosure of a formulation. (4) Test methods generally are not translated into design data. Chemical and molecular evaluation need to be carried out with the ultimate goal of a meaningful correlation with the mechanical results. (5) There is no universal, reliable mechanical adhesive test. (6) There is no reliable non-destructive adhesive test.

The solution to these problems, many of which are concerned with the characterization of the polymer adhesives, should provide the needed quality assurance and allow the further development of design and manufacturing techniques which are required to extend the adhesive bonding concept to the primary airframe structure.

INSTRUMENTAL RESIN CONTROL SCHEME

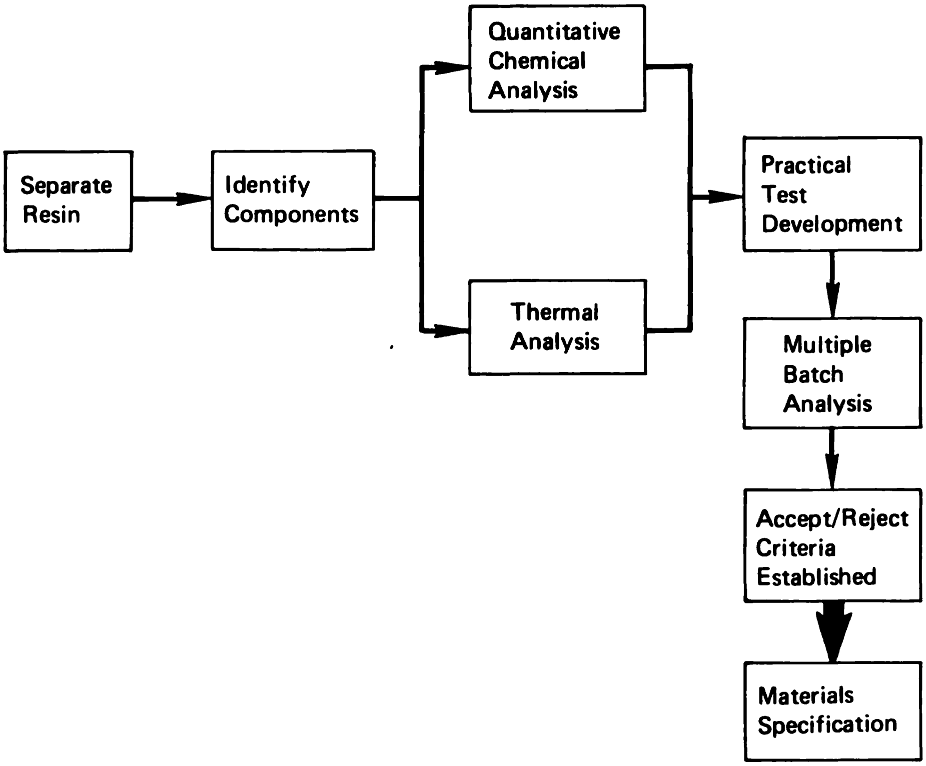
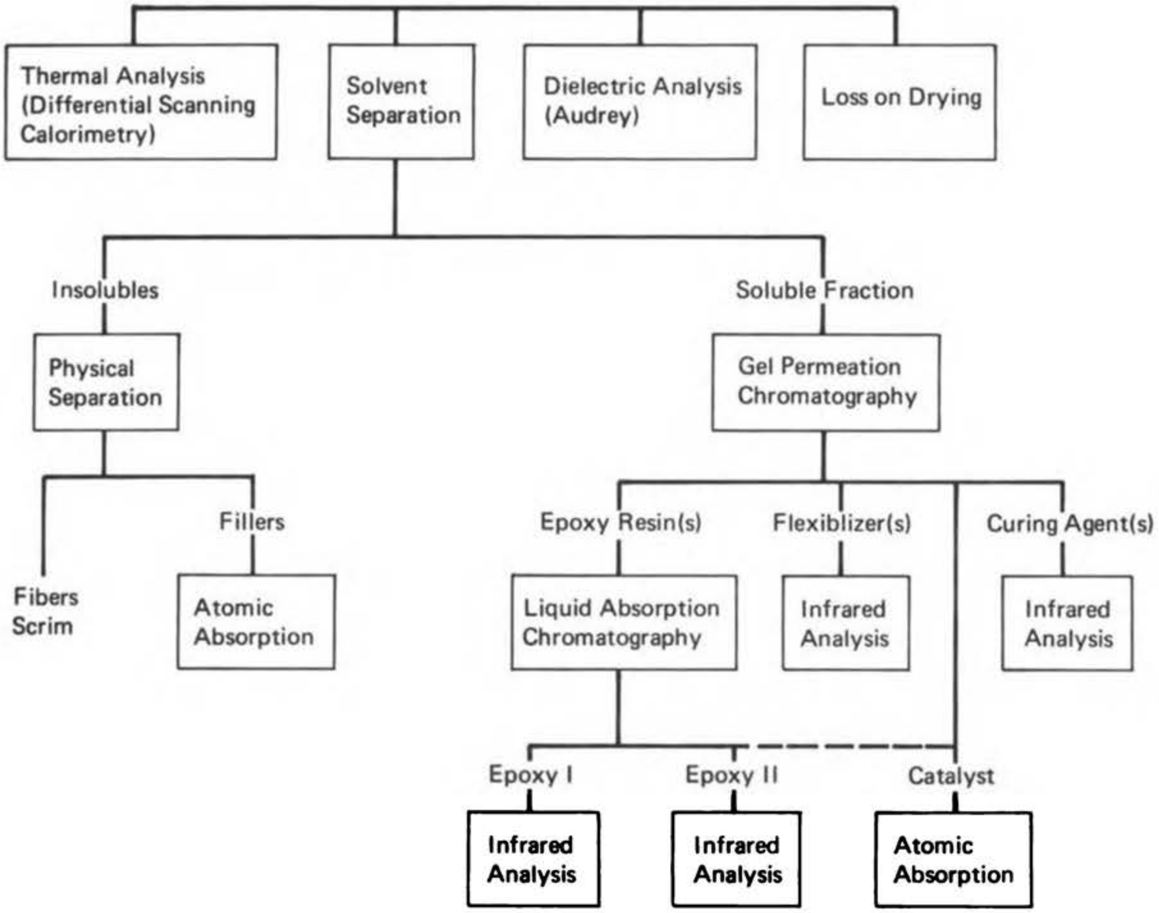


Figure 4



RESIN SYSTEM SEPARATION AND IDENTIFICATION

BORON/EPOXY PREPREG *STRUCTURAL ADHESIVE*

GRAPHITE/EPOXY PREPREG

Figure 5

APPENDIX A
McDonnell Douglas
Process Specification
Acceptance, Reinspection and Storage of Structural Adhesives

Commercial Designation ㉑	P.S. 11308 Type	Storage Temperature ①	Shelf Life (Months) ②	Primer Cure Cycle		Primer Application		Adhesive Cure Cycle			Overlap Shear (psi) (Minimum each Specimen)	
				Time	Temp	Dry Film Thick-ness	Add. Appl. Details	Time Min.	Temp	Press. (psi)	Room Temp	Elevated Temp ③
AF-32 (EC-1459 Primer)	None	40°F or Below	6	1 hr/ 30±10 min	R.T./ 175-200°F	–	–		250°F Type	10-15	500	–
AF-130 (EC-2333 Primer)	None	40°F or Below/ Ambient	6/12	30-40 min/ 45±10 min	R.T./ 130-150°F	0.0001- 0.0003	④		350°F Type	20±5	2250	–
AF-126-2 (BR-127 Primer) ⑤	None	0°F or Below/ 40°F or Below	6 ⑤	min 30 min/ 60±5 min	R.T./ 245-265°F	0.0002- 0.0004	⑥		250°F Type		3900 ⑦	–
AF-126-2 (EC-3903 Epoxy Pour Coat)	None	0°F or Below/ 40°F or Below	6 ⑤	min 30 min/ 30±5 min	R.T./ 180±10°F	0.0005- 0.0020	⑧		250°F Type		3900	–
AF-3002 Foam	XXVI	40°F or Below	6	–	–	–	–		350°F Type		1000	–
AF-3015 Foam ⑤	None	0°F or Below	6 ⑤	–	–	–	–		250°F Type		1000 ⑨	–
FM-37 Foam ⑤	None	0°F or Below	6 ⑤	–	–	–	–		250°F Type		1000 ⑨	–
FM-47 Type II (FM-47 Primer)	None	40°F or Below	6	min 18 hrs/ 60±10 min	R.T./ 220-240°F	0.001- 0.002	⑥		350°F Type		3000	–
FM-61 (BR-227A Primer)	XIX	40°F or Below/ 40°F ⑩	6	min 30 min/ 60±10 min	R.T./ 140-170°F	0.0015- 0.0025	⑥		350°F Type		2250	900(340-360°F)
FM-96	XXI	40°F or Below	6	–	–	–	–		350°F Type		2700	1000(340-360°F)
FM-960	None	40°F or Below	6	–	–	–	–		350°F Type		2700	1000(340-360°F)
FM-97	XI	40°F or Below	6	–	–	–	–	60-130 min	260±10°F	15-30	1500	–
FM-123-2 (BR-123 Primer) ⑤	XXXI	0°F or Below/ 40°F or Below	6	⑫	⑪	0.001- 0.0003	⑥	60-70	250°F Type	15-20	3600 ⑦	–
FM-123-2 (BR-127 Primer) ⑤	None	0°F or Below/ 40°F or Below	6	min 30 min/ 60±5 min	R.T./ 245-265°F	0.0002- 0.0004	⑥	60-70	250°F Type	15-20	3600 ⑦	–
FM-1000	XXII	40°F or Below	6	–	–	–	–		350°F Type		5000	–
HT-424 ⑤	VI	0°F or Below	4	–	–	–	–		350°F Type		2250 ⑦	1350(490-510°F)
HT-424 Type II Foa- ⑤	None	0°F or Below	4	–	–	–	–	40-60	350°F Type ⑫	20-50	450 ⑨	–
HT-432 ⑤	XXXIII	0°F or Below	4	–	–	–	–		350°F Type		2250 ⑦	1350(490-510°F)

APPENDIX A CON'TD

HT-435	⑤	XX	0°F or Below	4		-	-	-	-		350°F Type		2000	⑦	1800(490-510°F)
HT-424, HT-432 or HT-435 (HT-424 Primer 30%)		None ⑮	Ambient ⑮	6	⑤	30 min/ 60±5 min	R.T./ 140-160°F	-	⑬		350°F Type			⑭	-
MMS307 Type I and IV (MMS307 Type II Primer)		XXXIV	0°F or Below/ 40°F	4		30-60 min	200±25°F	⑯	⑥	60-70	350°F Type	45-55	2600	⑰	2000(355-375°F) 1500(410-430°F)
MMS307 Type III		None	0°F or Below	4		㉒	㉒	㉒	㉒		㉒			⑱	-
Plastilock 655 (Plastilock A526B or A1272B Primer)		None	40°F or Below/ 40°F ⑲	6		30±5 min	190±10	-	-		350°F Type		3000	⑳	900(340-360°F)
AF-106		X	40°F or Below	6						60-70 min	340-360°F	25-50 psi	1800		500(395-405°F)

APPENDIX A CON'TD

NOTES:

① Ambient means shop environment (no temperature or humidity control).

② When two materials are in the Commercial Designation column, the shelf life column will have only one number if both the same, and two numbers (in same order as materials) if different.

③ Numbers in parenthesis represent the test temperature.

④ Shake the EC-2333 primer for a few seconds before application.

⑤ Adhesive must be aged 24 ± 6 hours at room temperature prior to curing. After the adhesive is removed from the roll or sheet, protective wrap for 24 ± 6 hours before using or, if applicable, the adhesive can be applied to the test panels, assembled and held at room temperature in this condition for 24 ± 6 hours. Aging required for both acceptance and reinspection testing.

⑥ Mix the primer thoroughly for 5-10 minutes immediately prior to application.

⑦ See 6.6 for additional testing requirements for 0.080 lb/ft^2 adhesive. Flatwise tensile specimens are also required for adhesive acceptance for honeycomb core bonding in accordance with the requirements of 6.6.2.

⑧ Mix EC-3903 thoroughly for 5-10 minutes.

⑨ Foam must also meet the expansion and volatile requirements of 6.8.4.

⑩ Do not store below 25°F.

⑪ Air dry for 2 hours or force dry for 20-40 minutes at 150 ± 10°F.

⑫ Shim panels to provide a 0.032 inch foam thickness and to prevent excessive squeeze-out (See Figure 3). Do not use vacuum.

⑬ Prepare the HT-424 primer by thoroughly mixing the Part A and Part B components, then combining using a ratio of equal parts by weight.

⑭ Strength values are the same as for the respective adhesives without primer.

⑮ This is for the primer only. See the respective adhesives for their values.

⑯ As specified in MMS307.

⑰ In addition, qualify BR-400 primer (MMS307 Type II) and FM-400 film adhesive (MMS 307 Type I) to the analytical requirements of MMS307 using the following procedures:

(1) Select a container of BR-400 primer at random from each manufacturer's batch and test a portion of the contents. If the primer failes the test, one retest is allowed. Reject the batch of primer if it fails the retest.

(2) Select a roll of FM-400 film adhesive at random from each manufacturer's batch and test an end portion 6 inches by 24 inches in size. If the adhesive fails the test, remove a portion approximately 10 feet from the end of the roll that failed, and retest. Reject the batch of adhesive if it fails the retest.

⑱ No lap shear specimens required. Acceptance test foam adhesive by conducting sandwich beam shear tests per 6.8.3 and foam tests per 6.8.4. Also qualify FM-404 foam adhesive (MMS307 Type III) to the analytical requirements of MMS307. Test one sheet of foam adhesive, selected at random from each manufacturer's batch. Reject the batch of foam adhesive if it fails this test and one retest.

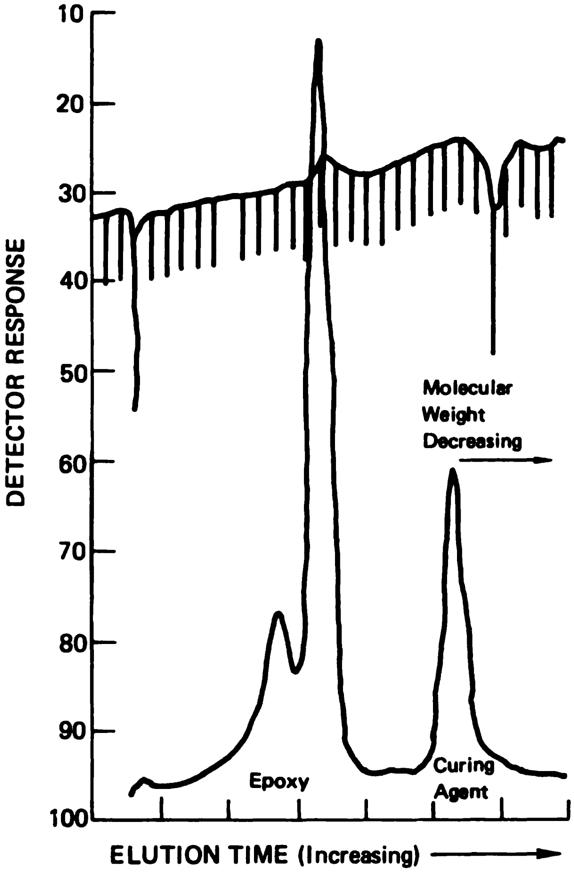
⑲ Do not store below 33°F.

⑳ Plastilock primer A-526B or A-1272B may be used with Plastilock 655 for acceptance testing and reinspection testing.

㉑ When more than one material is listed, the material in parenthesis is the primer for the material listed to its left.

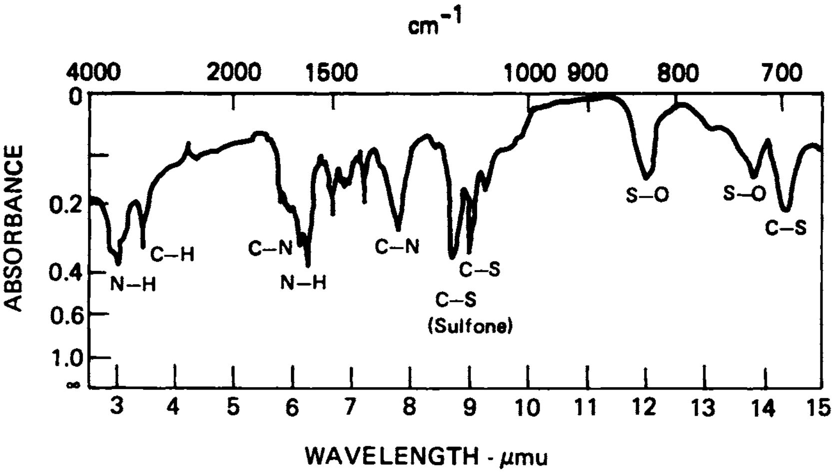
㉒ Follow the procedure of 6.7.

APPENDIX B

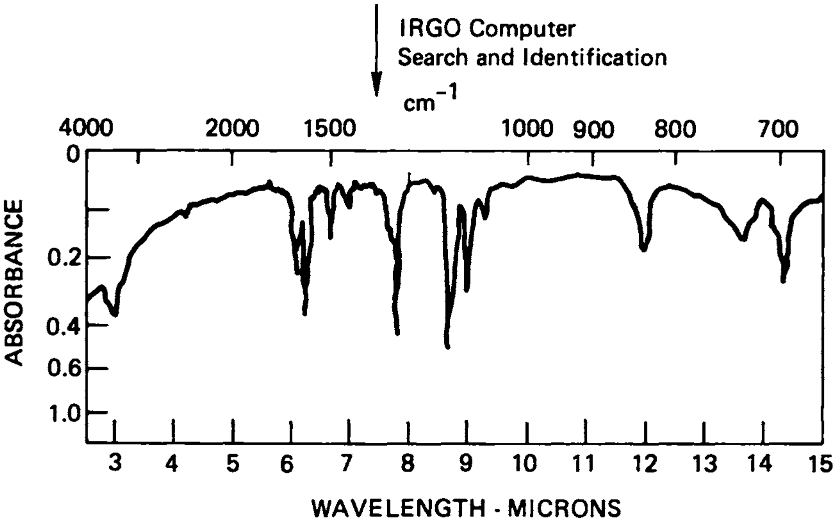


GPC SEPARATION

INFRARED SPECTRUM FOR UNKNOWN GPC FRACTION
from Graphite/Epoxy Resin



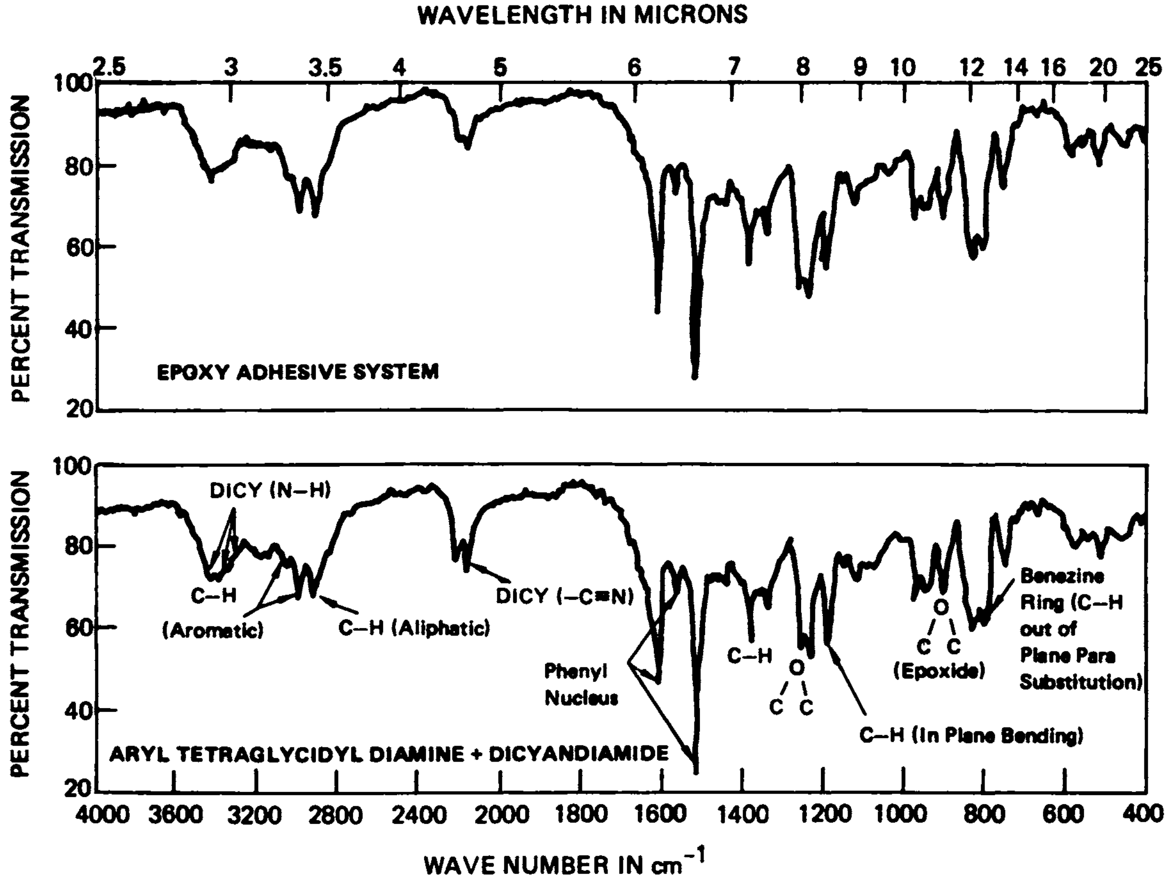
INFRARED SPECTRUM FOR 4,4′ DIAMINODIPHENYL SULFONE
Trade Name CIBA Eporal

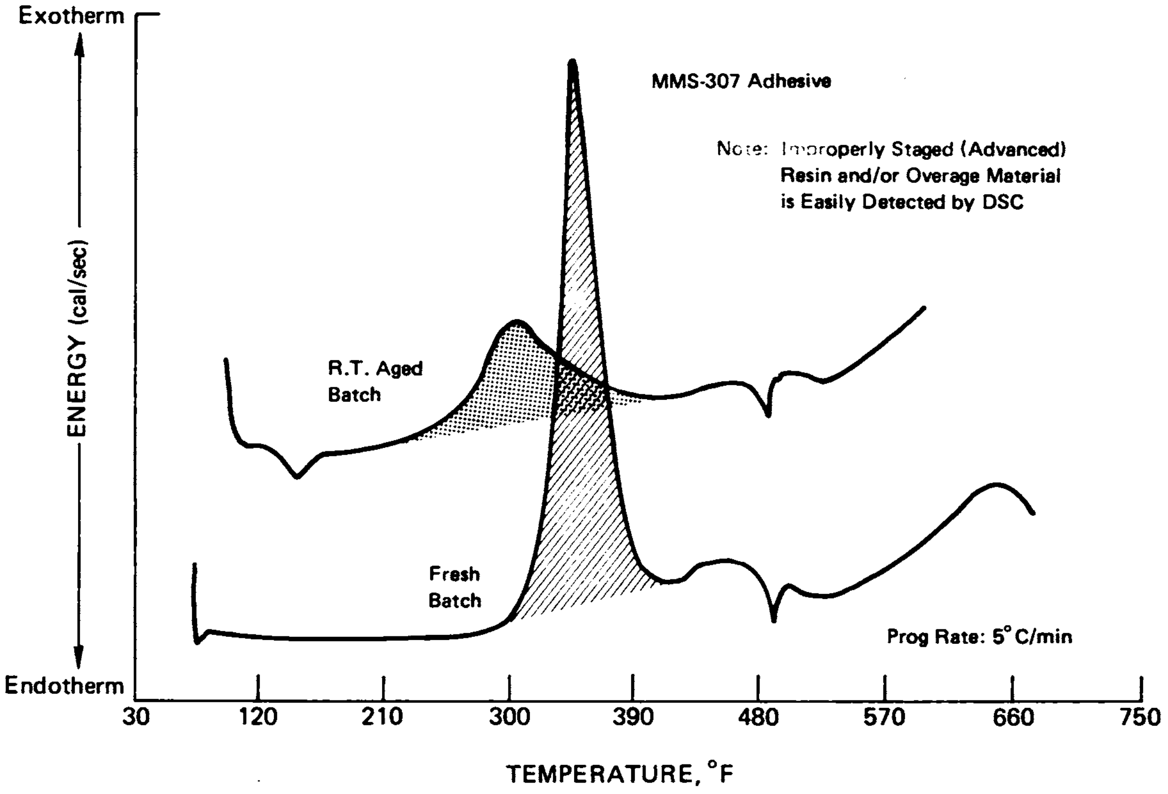


IR IDENTIFICATION

APPENDIX C

INFRARED SPECTRUM OF SYNTHETIC MIXTURES





Note: Improperly Staged (Advanced) Resin and/or Overage Material is Easily Detected by DSC

APPENDIX D

ANALYTICAL CHARACTERIZATION DIFFERENTIAL SCANNING CALORIMETRY (DSC)

REFERENCES

1. Boeing Commercial Airplane Company AFML-TR-75-TR-75-3, February 1975. "Durability of Adhesive Bonded Joints".
2. a) Lockheed Missiles and Space Co., Inc., AFML-TR-76, under contract No. F33615-75-C-5136. "Exploratory Development of Chemical Quality Assurance and Composition of Epoxy Formulations".
   b) Lockheed Missiles and Space Co., Inc., AFML Contract F33615-76-5170. "Dielectric Monitoring of the Adhesive Bonding Process".
3. McDonnell Aircraft Co., McDonnell-Douglas Corp., NASC Contract N00019-76-C-0138 "Quality Control of Structural Non-Metallics".

2. TRANSPARENT AIRCRAFT GLAZING

INTRODUCTION

The technology of producing and testing transparent aircraft glazing is a broad and complex subject, which in its totality is far beyond the scope of this case study. The major interest in this case study was to explore the role characterization plays in this technology. In presenting the results of this study, just enough background material has been added to make the uninitiated reader familiar with the current status of the field. To accomplish this, the discussion is started with the section on Current Materials and Constructions, and on Current Methods of Fabrication.

Information for this case study was gathered by personal contact (letter, telephone or visit) with individuals involved at every stage of the fabrication and testing of aircraft glazings, from the raw materials supplier to the end user. As this process progressed, the writers of this case study were able to formulate opinions about the philosophies behind the technology which dictate matters of requirement and specification. With an understanding of these philosophies, discussed in the section on Requirements and Specification Philosophies, the major results of the survey is found in the Sections on Test Methods; Questionnaire and Responses; and Problem Areas.

Since the Committee was concerned with present and future applications of characterization, it seemed advisable to include a short section on Advanced Materials and Designs before ending the case study with Conclusions and Recommendations.

Throughout the investigations, all of the individuals contacted were very helpful in supplying general information, but understandably reluctant to divulge details of glazing materials and their assembly. The case study writers did try to extrapolate from personal experiences. For this reason many of the views expressed in this case study must be considered as those of the authors and are not attributable to any one individual or company.

CURRENT MATERIALS AND CONSTRUCTIONS

The requirements for aircraft glazings, for example the windshields of supersonic military aircrafts, tax the properties of plastics to their limits. To excellent optical properties (high transmittance, freedom from haze and distortion of line of sight) must be added outstanding impact strength (for example, with birds at supersonic velocities), retention of properties over a wide temperature range, and many more.

Those functional requirements of aircraft glazing cannot be met by any one monolithic construction. Consequently, it has become necessary to design and fabricate glazings as composite laminar structures. The multilayer structures comprise such features as exterior coats for abrasion resistance, electrically heatable layers for defrosting, glare control layers, alternating hard-soft layers for energy absorption, edge coatings for barrier or chemical protection, and many others.

Finished products are complex and costly and the component ingredients vary from the mundane to the exotic. A reasonable guess would have the finished construction selling for more than ten times the cost of the components. Thus, one is dealing with a highly engineered product comprised of a number of different materials, each of which should be custom made of the finest quality available. However, the dollar sales volume for the individual components is, in general, too small to justify major expenditures on the part of the manufacturers.

The three basic transparent sheets used in the construction of aircraft glazing are glass, acrylic (poly(methyl methacrylate) - PMMA) and polycarbonate (bisphenol-A polycarbonate - PC). The fabricators shape and bond multiple sheets of one or more of these three transparent materials using their own adhesives, flexible interlayers, glass coupling agents, conductive coatings, functional layers, edge sealants, etc. The laminate fabricators use a combination of proprietary ingredients and manufacturing trade secrets to enable them to be competitive. The proprietary trade secret aspects of the manufacturing process obscure characterization of the components and their interactions with each other. A further consequence of the proprietary cloak over the manufacturing process is that there is probably little interchange of characterization data at intermediate stages of construction. The prototype for each design is subjected to extensive mechanical and optical testing. The final assemblies are of necessity checked only for optical properties, due to the destructive nature of most mechanical testing.

MATERIALS

ACRYLICS

Acrylic plastics, almost always used in the biaxially oriented form known as "stretched acrylics" are the most commonly used material of construction for aircraft glazing. They were introduced in 1936 and were used in World War II military aircraft. Stretched acrylics, glass and combinations of these two currently satisfy the requirements of the total civilian aircraft glazing market. Acrylic technology has had sufficient history to have reached a state of proficient application approaching the limits in ultimate properties of the polymer. Optical quality sheets are normally cast (bulk polymerized) one at a time from purified monomer between sheets of polished glass. As-cast acrylic sheets are essentially flawless, have excellent weatherability and high light transmission, but soften at 100-110°C and are rather brittle. They may be significantly toughened by means of biaxial orientation at somewhat elevated temperatures.

POLYCARBONATES

Polymers derived from bisphenol-A and phosgene were introduced as injection molding compound in 1960 and as sheet in 1965. This particular polymer is the only member of the polycarbonate family which is currently manufactured and processed in large volume. The polymer is made by a condensation process using a modified interfacial polymerization technique, and requires multiple operations to isolate the polymer powder or pellets. The PC particles are then formed into sheet by a continuous thermal extrusion process. The process exposes the product to much heat in the presence of air, and there are many opportunities for it to become contaminated. The optical quality is good but it probably will never consistently approach that of cast acrylics. Polycarbonates are naturally tough and do not require orientation, have a high heat distoritión temperature (135-145°C), require stabilizers for weatherability, and are combustion resistant. Polycarbonates, like PMMA, must be coated to improve abrasion resistance when exposed to wear conditions.

GLASS

The technology of glass is very old, and the products have essentially reached perfection within the limits of the basic materials. The key deficiencies of glass for aircraft glazing include its high specific gravity and inherent brittleness. Glass does provide the most abrasion and weather resistant transparent material obtainable.

COMPOSITES

Poly(vinyl butyral) PVB is synthesized by effecting controlled partial reaction of n-butyraldehyde with poly(vinyl alcohol). The resulting polymer contains a balance of pendant hydroxyl groups (which promote adhesion to glass) and cyclic butyral substituents. In its unmodified form, PVB is a relatively tough resinous material with few properties which would suit it for use as a safety glass interlayer. However, it is readily plasticized by assorted ester fluids to yield, when sheeted, a very tough, stretchable interlayer for safety glass. The use of PVB as an interlayer for automotive safety glass has a long history. The principal difference between the PVB used in automotive windshields and aircraft glazing is the amount and type of plasticizer employed. Automobile safety glass can tolerate a higher degree of plasticization since the temperature extremes to which automotive windshields are exposed are much more moderate than those for aircraft glazing. A combination of increased plasticizer content and increased temperature converts PVB to a weak, easily extended film. Under-plasticization and low temperatures cause PVB to be somewhat brittle. Thus it is necessary to compromise on performance at one end or the other of the temperature scale.

Silicone polymers are particularly attractive for composite interlayers since their extensibility and flexural moduli are essentially constant over wide ranges of temperature. Another good feature is their outstanding resistance to ultraviolet radiation. On the negative side, most silicones are relatively weak and are better known for their natural release ability rather than superior adhesion. Proprietary formulations are used in aircraft glazings.

A very tough silicone-polycarbonate copolymer developed by the General Electric Company has found use in bonding bullet-resistant polycarbonate laminates and glass-polycarbonate composites.

A proprietary polyurethane (PPG-112) developed by the Pittsburgh Plate Glass Industries reportedly combines many of the best features of PVB and silicones to yield a superior flexible interlayer with improved thermal capabilities.

Monsanto Research Corporation has recently been assigned U. S. Patent 3,923,757 which discloses a superior glass-polycarbonate adhesive interlayer. The interlayer comprises a partially crosslinked terpolymer of ethylene, vinyl alcohol and vinyl acetate. The terpolymer is prepared by partial hydrolysis of an ethylene-vinyl acetate copolymer.

CONSTRUCTIONS

Most of the information on typical military aircraft windshield constructions was obtained in an interview, regarding aircraft canopies and windshields with Mr. Robert Wittman, Prototype Division, Air Force Flight Dynamics Laboratory, Wright-Patterson Air Force Base, Ohio. Mr. Wittman's laboratory is concerned with end products such as windshields, and has the mission of devising constructions with good resistance to bird impact damage. His own experience has largely been with the materials used in such windshields.

Typical windshields are 1" to 1¼" thick and consist of multilayer laminates in which rigid (acrylic or polycarbonate) layers are alternated with rubbery or viscoelastic layers (poly(vinyl butyral) or PPG's No. 112 polyurethane). Adhesives may or may not be used between the layers; this and the nature of any adhesives are tightly guarded trade secrets. Usually the windshield has a thin layer of glass on the outside for abrasion resistance, and a layer of acrylic on the inside.

The F-111 has a new windshield design in which a glass laminate is replaced with one containing five rigid plastic layers and four interlayers. Three polycarbonate sheets are used in the interior of the sandwich and two acrylic face sheets are used with PPG's No. 112 polyurethane interlayer, for a total of 9 plies. There is also thought to be an adhesive involved. Windshields such as these can deflect as much as 4" on impact without shattering. Previous windshields were made of glass/silicone and were not resistant to bird impact. There is, of course, an additional problem of secondary images from the many interfaces in the complex laminates.

The B-1 bomber has unusually large windshields, which compounds the design problems. Currently a face layer of 0.050" chemically strengthened glass is used on the outside, curved cold and clamped in place. An optically perfect seal between the outer abrasion resistant glass facing the inner mechanically tough multiple laminate must be provided. A flexible adhesive interlayer is used for this purpose. Direct adhesion between glass and rigid plastic would be difficult to accomplish and would be disastrous insofar as performance is concerned. Differential thermal expansion coefficients could cause failure in either the bulk phase of the glass or plastic or at the interface on thermal cycling. Even if this expansion mismatch could be resolved, a failure in the glass could be transferred directly to the rigid plastic substrate.

The role of the flexible interlayers may be appreciated if one is aware that inorganic glass and most polymers existing in the glassy state are notch sensitive. That is, notched or scratched specimens tend to fail when flexed or under impact. If one adhers a strip of glass (or polymer with low elongation) by means of a rigid adhesive to a strip of polycarbonate which is normally tough and ductile, the combination may readily be broken by bending in the direction which puts the glass under tension. If one bends the specimen in the other direction, the glass alone will fail. Similar embrittling effects may result from applying thick scratch-resistant hard coats to normally ductile plastics.

The ultimate design of the windshield is in part dictated by the limitations of the materials involved. For example, bending a large sheet of thin glass to rigid tolerances and insuring adhesion to an inner layer of plastic presents a major challenge. Differences in thermal coefficients of expansion further complicate the situation.

Poly(vinyl butyral) is still used extensively in glass or plastic laminates because of its proven impact resistance. It is not, however, compatible with polycarbonates. Impact resistance is of particular interest in Mr. Wittman's laboratory since their objective is to design structures capable of withstanding high speed bird impact. Unfortunately, poly(vinyl butyral) tends to embrittle at low, and soften at high, temperatures. It is possible to minimize the high temperature softening by reducing the proportion of plasticizer used in the poly(vinyl butyral). This modification aggravates the low temperature embrittlement. The solution is a compromise in which heaters are incorporated in the composite to maintain toughness despite very low external ambient temperatures.

Transparent laminates are warmed by means of electrical resistance heating. In the case of glass, one has a relatively easy approach since optically transparent and conductive tin oxide films may be applied directly to the glass. In plastic laminates, a conductive thin gold film must be used and this reduces the transmittance.

The Air Force would like windshields to last about 6000 hours, the average airplane lifetime. To qualify for this lifetime, the windshields would have to pass qualifying tests for four times that life. In fact, lifetimes of 1000-2000 hours are commonly accepted if the plane is frequently used. Life testing includes heat cycling, with the heat applied by radiant heating or possibly hot air. Liquid nitrogen is used to introduce thermal shock. The whole set of problems associated with "accelerated" testing and the need to test whole structures as well as the windshields (because of transmission of load to the airframe) must be considered.

The Air Force is generally satisfied with the various currently available interlayers, including the proprietary ones. The PPG polyurethane can be used to 175-180°C for under 5 minutes, and is the only high-temperature interlayer available in sheet form. This is considered essential; cast-in-place interlayers have not worked well in multilayer laminates. The PPG material cannot be purchased in the open market (PPG will only make and sell laminates or windshields), nor can the other proprietary interlayers.

Acrylic and polycarbonate plastics are bought to MIL specifications, but these are not tight ones. They were originally developed only to identify a material by simple mechanical and physical property tests, and they offer no control over the ingredients going into that material.

Windshield specifications are set up as follows: the Air Force issues a set of requirements, largely optical, such as maximum distortion, minimum transmittance, etc. The windshield manufacturer writes detailed specifications and optical inspection techniques, and the Air Force uses these if they later purchase windshields directly. Flammability is not controlled since it is not an overriding consideration in comparison with other requirements already necessitating many compromises.

Both acrylic and polycarbonate sheet are frequently coated to improve their resistance to optically destructive abrasion and scratching. The most common approach consists of applying a very hard coating which resists abrasion as a consequence of its being harder than the common abrasive media. The alternative and less widely used approach consists of applying coatings which are extremely tough and flexible. The latter type coating may deform and bounce back when struck by abrasive particles. Polyurethanes have found some application in this category.

The material of choice for hard coatings is silica or silicates, which have been proven satisfactory in the form of glass. Siliceous material may be converted in situ to silica rich coatings. "Abcite" coated plastics which might fit in this category have been supplied by duPont. Owens-Illinois has a silica rich coating, and more recently Dow Corning has announced a scratch resistant coating which is predominantly silica. Sierracin has produced hard coats by direct evaporation of silica onto plastic. Another promising new development is plasma evaporated glass. All of the hard coat approaches require a delicate balance between sufficient thickness to provide the desired abrasion resistance, sufficient thinness to preclude notch sensitization of the plastic, and excellent adhesion.

CURRENT METHODS OF FABRICATION

SUPPLIERS AND FABRICATORS

Plastics used in aircraft glazings are purchased by fabricators from a small number of companies: acrylics from Rohm and Haas and Swedlow, polycarbonate from General Electric, polyurethane from PPG Industries, poly (vinyl butyral) from Monsanto, silicone resins from several sources, and glass from Corning. There are a few other minor materials used, such as fiberglass-filled acrylic or polyester around the edges of a windshield for support out of the optical line-of-sight areas.

These materials are fabricated into finished parts such as windshields by, again, a small number of companies. Parts using glass are supplied only by PPG Industries and Libby-Owens-Ford. The only fabricators of plastic laminations are Goodyear Aerospace, Swedlow, Sierracin, Texstar, and PPG. There is very little foreign purchase, except for a few windshields from Triplex, Pilkington's fabricator.

DESIGN AND PRODUCTION PROCEDURES

Because of their relative importance to this report, the remarks in this case study are restricted to military aircraft. The Military initiates the design process by generating mission requirements and performance parameters, and issues a request for quotation to which the aircraft manufacturers respond. Depending on the response the windshield or canopy is considered.

The actual canopy design can be achieved in one of two ways. Fifteen years ago the airframe manufacturer might have restated the requirements to the canopy fabricator and let him design the canopy. Now, however, the designs are so sophisticated that few, if any, fabricators have the capability of carrying out the design. Further, there is a great reluctance on the part of the airframe manufacturers to let the design of this critical assembly out of their hands.

Therefore, today the airframe manufacturers essentially design the canopy or windshield in complete detail. They then provide the fabricator with specifications consisting of production drawings detailing the configuration, materials, dimensions, and performance requirements, including such matters as edge attachments, bonding, and other details.

Qualification testing is done by the airframe manufacturer at his own location, since often the entire forward fuselage section is involved as well as the windshield. The tests include a spectrum of fatigue procedures, cycling in temperature and pressure and burst or impact testing.

REQUIREMENTS AND SPECIFICATION PHILOSOPHIES

As pointed out several times in the Committee report, the goal of every purchaser insofar as characterization is concerned is to be able to specify a material completely, so that its performance can be guarenteed unequivocally. The need for realistic compromise in reaching this goal is discussed elsewhere. It was of interest in this case study to explore the nature of the requirements which purchasers of materials, fabricated transparencies, and airframes containing them place on their suppliers; and particularly, the extent to which specifications for these items are based on realistic compromises. Our findings are reported in terms of general philosophies rather than specific details.

MATERIALS SPECIFICATION PHILOSOPHY

The major components of any aircraft composite glazing are glass, PMMA, PC, or selected combinations of these. Based on familiarity and history of performance, glass is glass and seldom presents new problems. PMMA is likewise rather well understood and presents few problems or surprises.

Polycarbonates are relatively new to the application and do present many real or imagined problems.

Glass is used where maximim abrasion resistance is required; PMMA is used where it will meet the temperature and toughness requirements; and PC, where PMMA is not satisfactory. The other component materials are primarily specified on the basis of functional performance rather than their chemistry.

In cases where finished canopies fail to meet optical or mechanical specifications, the fabricator's natural reaction is to place the blame on the materials. The material suppliers would fault the fabricators. Neither reaction addresses the real problem of setting initial specifications on each component and predetermining the effects of interactions between materials and processing conditions on the maintenance of these initial specifications.

PC offers a particularly pertinent case for consideration. Optical properties are not consistently as good as those of the more familiar PMMA. Optical defects sometimes occur spontaneously during thermal processing. This supposedly very tough material occasionally becomes embrittled. Unexplained crazing may occur. The fabricator would like to be able to place all responsibility for performance in the hands of the material supplier. Unfortunately the supplier does not know or cannot even guess what combination of chemical and mechanical stress will be applied to his product. For example, mechanical properties of polycarbonates fall off rapidly as the molecular weight decreases below a critical value. Ordinarily the polycarbonate vendor will supply sheet of adequate molecular weight to provide the required balance of properties and processability. Certain combinations of moisture and heat encountered in the fabrication process may cause sufficient reduction in molecular weight of the polymer to cause it to embrittle without any optical evidence of degradation. Thus, a canopy weight might pass optical inspection and fail in the field when subjected to mechanical stress.

One can easily get the impression that most of the testing is of a mechanical type but failures are blamed on the chemistry.

FABRICATION SPECIFICATION PHILOSOPHY

The ultimate specifications on a fabricated transparency are based on a set of largely optical performance requirements such as maximum distortion and minimum transmittance. The mechanical requirements are assumed to be met if prototypes successfully passed rigorous physical testing.

The frightening thing is that a given structure may meet optical specifications but be in a very weak mechanical condition, as a consequence of either incorporation or poor quality material or material degradation due to poor assembly practices. The fabricator frequently processes several small pieces (coupons) in parallel with the canopy or windshield but these coupons have only identical thermal history. The mechanical stresses resulting from forming processes, or differential expansion of large versus small parts, can obscure the facts. If the coupon fails mechanically, the canopy probably will also. If the coupon passes, the canopy still may not.

QUALIFYING TEST PHILOSOPHY

The principle which appears to be followed by the airframe manufacturer in testing fabricated glazings includes rigorous mechanical testing of prototypes and total assemblies. This includes fatigue testing, cyclic temperature and pressure testing, burst and impact testing, and optical testing. If the design meets the requirements, subsequent copies are then simply checked for optical conformity. Flammability testing is not routinely applied to aircraft glazing.

TEST METHODS

This section describes the full complement of characterization tests applicable to aircraft glazing materials and constructions, as transmitted to us by the Air Force Materials Laboratory, in response to the quentionnaire described in this chapter. Discussion of which tests are routinely performed and of problems arising from inadequate test methods is developed in later sections.

TEST SCHEDULE

The schedule of testing which would be desirable to characterize a plastic material for aircraft glazing use is described in Table I. Basically, the table lists four property groups versus two types of testing. Each of the property groups is subdivided into mechanical, optical, physical and chemical categories. As-received and after (conditioning) are taken as the two states of a material, with the latter subdivided into specific exposure conditions. The assigned numbers in the body of the table indicate how soon a particular combination of a test and a condition is conducted by a supplier or fabricator. A one (1) means an early evaluation and a five (5) a much later evaluation. The numbers reflect only a consensus of general ordering of the tests. The asterisks mark the tests and conditions considered most important. Letters at the left of the table identify the tests as functional or of a basic characterization nature. The functional tests are close to being standard throughout the industry--except for abrasion resistance where at least two differing from the Taber Abrader are required, i.e., rubbing and hard particle impact. The characterization tests are probably available, but are not used extensively. Both types are necessary and useful; however, the functional ones are usually the final criteria.

TABLE I Schedule of Characterization Testing

			Type Test After Conditioning (where appropriate)														
Property			None (As Received)	Accel. Weathering (Machine)	Accel. Weathering (Natural)	Elevated Temperature	Moisture Resistance	Temperature/Humidity	UV Radiation Resistance*	Thermal Cycling	Abrasion Resistance I Taber	Abrasion Resistance II Rubbing	Abrasion Resistance III Impact	Solvent Resistance	Low Temperature	Thermal Shock*	Hot Side/Cold Side
F	MECHANICAL	Tensile Strength*	1	3	3	1	4	4	2	5					3		NEED
F		Tensile Modulus	1	3	3	1	4	4	2	5					3		NEED
F		Tensile Elongation*	1	3	3	1	4	4	2	5					3		NEED
F		Flexural Strength	2	4	4	2	4	4	3	5					4		NEED
F		Flexural Modulus	2	4	4	2	4	4	3	5					4		NEED
F		Impact Strength I	1	2	3	5	4	4	2	5					3		NEED
F		Impact Strength II*	5	5	5	5	5	5	5	5					5		NEED
F		Fracture Toughness*	4	5													
F		Creep Rupture	5	5													
F	OPTICAL	Transmittance*	1	1	1	1	2	1	1	3	1	1	1	1			
F		Haze*	1	1	1	1	2	1	1	3	1	1	1	1			
C		Color*	4	4	4	4	4	4	4	4							
C		Yellowness Index	2	3	3	2	3	3	3	4							
C		Index of Refraction*	1														
F		Stress/Solvent Crazing											1				
C	PHYSICAL	Heat Distortion Temp*	1														
C		Glass Transition Tg	1														
C		Specific Gravity*	1														
F		Hardness	2	3	3	3	3	3	3	4							
C		Thermal Expansion*	2														
C		Thermal Conductivity	2														
C		Brittle Point													4		
F		Dimensional Stability				3											
C	CHEMICAL	IR Spectra	5														
C		UV-Vis Spectra	3														
C		DSC/DTA	5														
C		TGA	5														
C		Flammability	4														
C		Solubility												1			
C		Molecular Weight	5*														
C		Intrinsic Viscosity	5*														
C		Flow	3														
C		MW Distribution	5*														

TEST IDENTIFICATION

Table II identifies one or more test technique for evaluating each material property and the environmental condition to be used. Many of the tests are currently being developed or revised by the ASTM F7.08 Subcommittee on Aerospace Transparent Enclosures and Materials.

TABLE II Identification of Tests

PROPERTY TESTS	ASTM	FTMS 406	MIL SPEC	OTHER
Mechanical				
Tensile Strength	D-638	1011	-	
Tensile Modulus	D-638	1011	-	
Tensile Elongation	D-638	1011	-	
Flexural Strength	D-790	1031	-	
Flexural Modulus	D-790	1031	-	
Impact Strength I	D-256	1071	-	
Impact Strength II		1074	-	
Fracture Toughness	E-338	-	P-25690	
Creep Rupture	D-674	1063		
Optical				
Transmittance	D-1003	3022		
Haze	D-1003	3022		
Color	E-308 D-1544			
Yellowness Index	D-1925			
Index of Refraction		3053		
Physical				
Heat Distortion Temp.	D-648	2011		
Glass Transition Temp				
Specific Gravity	D-792	5012		
Hardness	D-785 D-2240	1083		
Coef. Thermal Expan.	D-696	2031		
Thermal Conductivity	C-177			
Brittle Point	D-746	2051		
Dimensional Stability	-	-	P-25690	
Chemical				
Intrinsic Viscosity				
Molecular Weight				
M.W. Distribution				
Flow	D-1238			
UV/Vis/IR Spectra				
TGA				
DTA/DSC				
Solubility	D-543	7011		
Flammability	D-635	2021		
Exposure Conditions				
Abrasion Resist Taber	D-1044	1092/1093		
Rubbing	-	-		
Impact	-	-		
Weathering Natural	D-1435			
Accelerated Weathering				
Machine	G-23	6023		
Natural				EMMA
Elevated Temperature	D-794			Desert
Moisture Resistance	D-570	7031		Sunshine
Temperature/Humidity		6011		
UV Radiation				
Solvent Resistance				
Low Temperature				

SPECIAL TESTS - HIGH SPEED IMPACT

The Air Force Flight Dynamics Laboratory described a number of tests in which, by using an air cannon, birds were impacted against actual windshields of the entire front of an aircraft fuselage. The Air Force views, as its major problem, stopping birds from penetrating the windshields of low-flying, high-speed aircraft.

QUESTIONNAIRE AND RESPONSES

To provide information for this case study where personal interviews were impractical, a questionnaire was sent to representatives of the Armed Forces and windshield fabricators. Replies were received by mail, and in some cases telephone discussions were held later. The following questionnaire, with minor variations, was used:

"In considering the characterization of materials for use in aircraft glazing, our Committee sees several groups of properties as important:

- Structural and mechanical, including tensile, flexural and impact strength, and creep behavior.
- Optical, including haze, transmittance, color and yellowness.
- Physical, including specific gravity, hardness, and a variety of thermal properties.
- Molecular, including molecular weight and related areas, various spectra, and morphology.
- Permanence and stability, including flammability, chemical and solvent resistance, oxidation, yellowing, surface deterioration, etc.

Do you see other groups of properties or specific properties that should be added to these lists?

For each group, or if appropriate for each property or material listed, would you comment as follows:

1. What tests do you use or recommend for characterizing the materials for these properties?
2. Are these functional tests (like many ASTM tests) or do they characterize the basic chemical, physical, molecular or morphological structure of the material? Which type of test is more useful to you?
3. Are you satisfied with available characterization tests in these areas? If not, what other tests or what test improvements would you like to see?
4. In your experience, should better control be provided over the basic molecular structure, chemical nature, physical properties, or nature and amounts of additives or impurities in these materials?

5. Do you feel that resin suppliers, in general, exert adequate quality control on the materials they supply for aircraft glazing?
6. Do you feel that the producers of enclosures, canopies, windows, etc., from these materials should characterize them further? If so, in what respect and by what tests? Have there been specific problems that better characterization could have solved? Please amplify.
7. Should the ultimate purchasers of the enclosures or the aircraft do further testing on delivery? Please amplify as in No. 6, if so.
8. What field problems are you aware of that better or more complete characterization might aid in solving?

Any additional comments would be much appreciated."

Answers to these questions came from the Air Force Materials Laboratory and the Air Force Flight Dynamics Laboratory, each representing the viewpoint of the ultimate purchaser; and from Texstar, a producer of fabricated transparencies. A second fabricator, Sierracin, sent material in reply that was only indirectly related to our questions, but a few comments from this company are included.

The Air Force Materials Laboratory provided detailed answers to Questions 1 and 2, in the form of Tables I and II. As indicated there, most of the tests are of the functional type and originate with the ASTM or military specifications. The comment was made that both characterization and functional tests are useful, but final decisions are based on functional tests.

The Texstar responders said that they run only certain optical tests, but rely on the resin suppliers to provide other test results useful for design data. Their trouble is that these data, such as those from creep or cyclic loading tests over a range of temperatures, are either not available or not meaningful.

Question 3 was meant to be directed toward characterization tests, but the replies invariably referred to functional tests which were unsatisfactory. The most complete response came from Textar. They spoke at length about the problem of testing for toughness and impact strength. The Izod and other standard tests are not meaningful, since they test the notch and not the material. (The questionnaire did not ask about tensile impact, which does not use a notched specimen.) The Gardner method does not discriminate between good and bad, and the falling dart test does not show up brittleness. Stretched acrylic testing has similar problems. There is a "K-factor" test using an artificial notch, but it is very operator dependent.

Texstar also mentioned abrasion testing as another problem. The Taber test is very poor, the problem being in the abrasion step rather than the optical measurement via haze. The abrasion part is dependent on wheel preparation, liquid used, and other operator variables. It is possible to get "any answer you want" but it does not measure real-life situations. Flow lines on a sheet cause the wheel to bounce and tear into the plastic.

A new Bayer abrasion test was thought by Texstar to offer possibilities, and said to be under test by ASTM. It appeared to involve a coupon in a tray with abrasion medium on top and a scrubbing or brushing operation.

Question 4 asked whether control of molecular structure and of the detailed composition of a product was necessary. The Air Force Materials Laboratory was emphatic: "The answer to ,Question 4 on the need for better control of material chemistry is a resounding YES! However, the nature of this industry makes this virtually impossible. Consider for example the acrylics: Several firms make their own monomer and they form as-cast and stretched sheet, while others buy available monomer to make sheet. In the first case molecular structure, chemical nature, additives, and impurities can be controlled, but in the second case little control is possible".

Other responders were less outspoken, but all the replies carried the implication that this information should be known. Texstar commented that they feel they need to know molecular weight and distribution. They sometimes get poor flow, and other problems arise such as distortion on forming blended materials. Melt viscosity measurement alone does not provide enough information. This is a problem with polycarbonate; acrylic is cast, and all they need to know is whether it is fully polymerized--i.e., free from inhibition by the colorants.

On the other hand, based on this and other responses it is surmised that most of the people who say they want this detailed knowledge of molecular structure parameters and chemical composition would not know what to do with it if they had it. What they really want is material that behaves the same way every time. They think that a detailed "fingerprint" of the material should allow them to tell in advance if this would be true. A difference in some structural or compositional parameter could be pointed to as evidence that the material was different and therefore behaved differently.

Question 5 asked whether the quality control at the resin producers was adequate. The answers varied. The Air Force Materials Iaboratory interpreted adequate to mean meeting minitary requirements, and said yes on the basis that these tests of mechanical and optical properties were normally met. The other responders said no. The fabricators were the more emphatic, dwelling on lot-to-lot variations, the need for them to spend time in the suppliers' plants preselecting material, the occasional occurrence of material meeting all specifications but still not performing properly, and many other complaints. They tended to blame performance changes on variations in molecular properties, when it would seem very difficult to find adequate reasons to expect this and when the properties in question had not been measured.

Question 6 carried on the inquiry in greater detail asking if the fabricators should test their incoming materials further to insure good quality and performance. The Air Force Materials Laboratory pointed out that this is done but primarily to provide processing data for various operations such as stretching, bonding, or machining. The Air Force Flight Dynamics Laboratory made the important observation that suppliers of materials to the fabricators should provide them, on a guaranteed basis, doing the characterization and taking the responsibility.

In Question 7, the questionnaire asked about the need for testing by the purchasers of the fabricated transparencies. Again it was pointed out that some testing is appropriately done. The users, however, evaluate the complete, often laminated transparency for properties closely related to the anticipated operational conditions to be encountered by the aircraft, such as pressurization and aerodynamic loads, bird and hail compact, aging, delamination, thermal distribution (heated panels), etc. There are always problems which are not apparent in the base material, or in the transparency, which become obvious only after a short time in service. Ice crystal abrasion, static charge buildup, and rain-erosion removal of coatings are examples.

In other respects, the answer to Question 7 was the same as to 6. That is, the fabricated parts should be provided on a guaranteed performance basis. In other words, the chain of supply should work in such a way that each link operates with complete reliance on and assurance from the preceding links.

Only Texstar took a different point of view. They did not expect their customers to have to do any testing of their products. They provide records of processing, verify the opticals, provide coupons which have followed the pieces through processing, and feel no more is needed.

Their problem is in circumventing the destructive testing of finished items. Although a coupon accompanies the item through the process, it only gets approximately the same heat history, and not the same stress history.

It is interesting to note that no responders offered evidence of field problems that might have been solved by better or more complete characterization. We can rationalize this in several alternative ways: (1) Perhaps there simply are no problems that involve characterization in this field. (2) Perhaps the problems solvable by characterization have already been solved. (3) Perhaps characterization is powerless to solve the problems that do exist. (4) Perhaps the understanding of what characterization can do to solve problems is lacking.

The latter possibility would appear most worthy of consideration. A thorough characterization of failed assemblies should be undertaken where materials of composition could have triggered the failure.

PROBLEM AREAS

This section is brief, since most of the people that were contacted failed to identify specific problem areas in which characterization might offer help. The ideas presented are largely those of the case writers.

ORIENTATION

Orientation and built-in stresses in transparencies can either contribute to toughness or predispose them to failure. For example, normally brittle acrylics may be toughened by means of biaxial orientation at elevated temperature. Toughened acrylic may also become brittle (as a consequence of relaxation) if exposed to somewhat higher temperatures. Polycarbonates are normally rather tough and may be further toughened by stretching. However, a component with irregular disposition of stress may fail disastrously, especially if exposed to hostile environments (solvents, amines, water vapor, etc.).

MOLECULAR-WEIGHT DEGRADATION

Polymer degradation, especially in polycarbonates, can lead to composites with excellent optical properties but marginal mechanical performance. Polycarbonates are condensation polyesters. The linkages between monomers are theoretically formed by removing water molecules, and the polymers may be degraded by re-inserting the water. Thermal processing of polycarbonate containing absorbed moisture, or processing of polymers in the presence of moist air, can cause some loss of molecular weight. This degradation does not exhibit any visually detectable symptoms unless the polymer is heated to very high temperatures or the water content is very high. In either of the latter instances, bubbling and frothing may be noted.

Essentially all thermal processing leads to some molecular weight degradation with the severity being determined by time, temperature, and moisture content. Properties tend to fall off gradually with decreasing molecular weight, and at a critical point fall off drastically. Visual appearance is frequently unchanged. Determination of intrinsic viscosities of polymer taken from processed samples could be used to assess processing damage, if any.

INTERACTIONS AMONG COMPONENT MATERIALS

Chemical interaction and compatibility testing between assorted materials of construction was not mentioned as the subject of any testing programs. Migration of plasticizers, stabilizers, residual monomers, solvents, coupling agents, and moisture across laminate boundaries could cause problems. It was felt that these possibilities should be explored.

ADVANCED MATERIALS AND DESIGNS

The military services are supporting a number of worthwhile ambitious programs aimed at raising the thermal operating limits of future aircraft. A recently assembled "Want List" from the Air Force Wright Aeronautical Laboratory is reproduced as Table III to illustrate the current thinking.

TABLE III Future Requirements for Aircraft Glazing Materials

Maximum Use Temperature	230 to 260°C	
Termal Gradient	190 to 200°C	
Thermal Shock	–40 to +260°C	
Heat Distortion Temperature	200 to 300°C	
Coefficient of Thermal Expansion	$<80 \times 10^{-6}$	
	Short Time	Long Time
Tensile Strength ambient	12-18,000 psi	–
Tensile Strength, 120°C	8-10,000 psi	6-8,000 psi
Tensile Strength, 260°C	5- 8,000 psi	3-6,000 psi
Tensile Elongation, ambient	10-75%	
Tensile Elongation, 120°C	>100%	
Tensile Elongation, 260°C	>200%	
Impact Strength, Izod	3 – >10 ft. lb./in of notch	
Impact Strength, Dart	8-12 feet	
Fracture Toughness	3-6 x 10^3 lb/in$^{3/2}$	
Transmittance	>90%	
Haze	<1%	
Color	Water white	
Index of Refraction	1.3 - 1.7	
Specific Gravity	0.9 - 1.4	

None of the individual specifications are beyond the capability of selected known polymers. However, the possibility of attaining all or most of them in one polymer presents a challenge which most probably will not be met in the near future. Fortunately, total solutions are not necessary for all applications, and the government is ready and willing to solve material problems one step at a time.

Advanced materials programs aimed at the distant future must realistically be considered. The significance of "distant future" can be appreciated if the history of polycarbonate applications in military aircraft is considered. Bisphenol-A based polycarbonates were discovered more than 20 years ago. They have been commercially available for 16 years and are currently produced at an annual rate exceeding 100 million pounds. Their first military aircraft application was as light housings on the trailing wing edges of the Lockheed F-104 Starfighter in 1960. Fifteen years later, material quality does fluctuate and fabricators are still reporting product and fabrication deficiencies.

When we consider the probable market for aircraft glazing with 260°C operating capability, the military emerges as the only customer. Even the supersonic Concorde transport uses an essentially all-glass canopy system. Polycarbonates, which offer significant thermal-mechanical advantages over acrylics, have not yet been utilized in commercial aircraft as a major glazing component. At the pace the polymer industry is moving, the chances of a fall out product for aircraft applications from the commercial plastic marketplace are very small.

Federally funded programs are attacking the problem of providing advanced materials research and development through internal agencies, industry, and academia. The most obvious approach is that of critically examining all new offerings of the polymer industry. Evaluation of the polysulfones of Union Carbide, 3M, and (more recently) ICI falls in this category. These materials have attractive thermal stability, some superior thermal-mechanical properties, and fair to good optical transparency.

A few comments on the background of polycarbonates derived from bisphenol-fluorenone (BPF) will illustrate the synthetic approach. The fact was known that bulky, sterically hindered connecting linkages between the two phenolic portions of a bisphenol lead to enhanced heat distortion temperatures in the polymers. Morgan[1] described a number of "all aromatic" polyesters and reported that the glass transition temperature (T_g) of the polycarbonate of BPF was 355°C. Inasmuch as there is a reasonably close relationship between T_g and heat distortion temperature of a given polymer, the BPF polycarbonates should meet or exceed the thermal requirements on the Wright Aeronautical Laboratory "Want List" (Table III).

All that remained to be done was to: (1) develop a source of supply for fluorenone, (2) produce the bisphenol in a state of high purity, (3) polymerize it, and (4) fabricate the polymer into useful forms.

The first three tasks could be accomplished with a reasonable degree of proficiency. The fabrication remains to be accomplished after several years' consideration, because the decomposition temperature is reached before the polymer softens sufficiently to fabricate. Powder metallurgy type fabrication or solvent casting of thin films is possible, but neither approach leads to useful glazing configurations.

The BPF polycarbonate program has subsequently been modified in a direction toward compromise. One may trade some of the elevation in T_g for a gain in processability and still have T_g higher than for bisphenol-A polycarbonate (150°C). The polymer chemist has many options, such as copolymerization, available for modifying T_g, and all are presently being explored. After the polymer is modified to yield a processable polymer with adequate T_g, other deficiencies will not doubt become apparent.

In addition to striving for one polymer with a perfect complement of properties, continuing research and development efforts are being directed toward combining existing materials into composites, where individual deficiencies are minimized and positive features maximized.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

There is a lack of sufficient understanding among individuals and companies of what characterization can be expected to do relative to transparent aircraft glazing. On one hand, the need for and usefulness of characterization--particularly of a chemical nature--is not recognized; on the other, the desire for characterization that will guarantee perfection is all too obvious.

Available materials are adequate for today's requirements, if the quality of the individual components is as good as it frequently is, and if the fabricators follow the best procedures they are capable of following. Problems may arise when material quality or processing procedures vary from the norm.

Secrecy among fabricators, which is necessary for their individual survival, frequently adversely affects the solution to many of their collective problems.

Design of canopies and windshields for aircraft incorporates a reasonable degree of technical sophistication. Actual construction or assembly approaches the skilled craftsman category. Application of polymer chemistry is almost non-existent throughout this industry.

There is a critical need for specialized non-destructive testing to insure adequate performance of compositions whose deficiencies only show up in service. Coupons which go through the same processing are a step in this direction, but are not fully adequate.

Everyone in the procurement chain, from raw material vendor to aircraft purchaser would like a "fail-safe" quality control system which would indemnify him and place the blame on his supplier. If polymer characterization or so called "molecular fingerprints" would serve this purpose, everyone would be in favor of implementation. However, realistic compromise approaches to this ideal have not been developed.

RECOMMENDATIONS

Continuing education (lectures, short courses, audio courses, etc.) should be developed with the objective of describing and demonstrating what characterization can accomplish; and strong encouragement should be given to those responsible for quality at all stages in the development of aircraft glazing to participate actively in this educational process.

If there are to be any advances in aircraft transparency composites, research and development support will be needed by the U. S. Government. If experience with bisphenol-A polycarbonate can be considered typical, the development costs and time involved will be extensive.

A study of the dynamic mechanical properties of polymeric materials for aircraft glazing use should be made, over the temperature and environmental ranges in which they are expected to operate, to provide information of help to designers.

A polymer characterization study (chemical and physical) of materials of construction for aircraft transparencies should be directed toward (1) materials to be incorporated in composites, (2) completed composites, and (3) failed composites.

Chemical characterization should be investigated, and meaningful analyses made part of coupon testing. Continuing attention should be placed on the development of non-destructive testing of fabricated transparencies.

The occurrence and importance of interactions among the materials used in transparencies, particularly directed toward potential boundary problems in laminar constructions, should be explored.

REFERENCE

1. P. W. Morgan, Macromolecules, 3, 536 (1970).

3. STRUCTURAL FOAMS

INTRODUCTION

Structural foams were selected for the study because of their potential as a more economical class of replacement materials for many items of concern to the military. The study discusses the advantages of structural foams, design limitations, applications, foam structure, test methods employed on the raw and foamed materials, and future needs. Also, it provides matrices showing some properties/influencing factors relationship trends of several foam systems. This information can be used as general guidelines in foam formulation and design R&D work.

BACKGROUND

Structural foams are of high density, always having a skin, and a density gradient from outside to inner core. These are different from rigid foams of uniform density which have densities of approximately 2 lb/ft.^{3}. The bulk of the industrial foam market (80%) lies in low density, flexible foams. Generally, there are three types of polymeric foams: (1) syntactic foams where a low density material is added to the compact plastic; (2) reticulated foams where the cells are 100 percent open; and (3) cellular foams where the cell is surrounded by a structure such that nearly 100 percent of the cells are closed. Unlike sandwich panels of foam material covered by reinforced skins, structural foams do not have a density discontinuity and therefore no shear plane. The entire structure supports flexure, compression, etc. For a given thickness, structural foams would not be expected to be stronger than a compact plastic; in fact all one can hope for is maintenance of the compact plastic strength properties. The great advantage of the structural foam is its lighter weight for a given thickness. Specific strengths in terms of rigidity for structural foams are approximately twice those of an equivalent compact plastic.

Through extensive trial and error a wide variety of items has been designed, fabricated, functionally evaluated, and commercialized when warranted. Once the prototype has been developed, then material property values are determined primarily for quality control and secondarily for the development of similar items.

ADVANTAGES OF STRUCTURAL FOAMS

GREATER STRENGTH TO WEIGHT RATIOS

With only a 25 percent increase in wall thickness, the structural foam has twice the rigidity of an equal weight solid plastic part. On an equal weight basis, e.g., a polycarbonate foam is twice as rigid as aluminum and five times as rigid as steel.

STRENGTH TO WEIGHT RATIOS

Ratio	Structural Foam	Aluminum	Steel
Stiffness to Weight	110	90	45
Flexural Strength to Weight	133	45	20

STRESS FREE MOLDING

Because the mold cavity is filled by the internal expansion of the material, very low inherent stress occurs in molded parts. This minimizes stress-crazing and cracking.

SIMPLIFIED AND LOWER COST PRODUCTION

Foam molding produces complex finished parts (including colored parts) in one operation. This eliminates many sub-assemblies, reduces total machine operating time, and lowers tooling costs. For example, the finished case for an MD 522A/GRC teletypewriter weighing five pounds would cost approximately $8 in mass production (contractor estimate) whereas the materials alone for the fifteen pound aluminum case would cost about $10.

DURABILITY AND LOW MAINTENANCE

Structural foam parts are, in general, long-lasting, and resistant to degradation (rotting, etc.). Their surfaces are non-porous; parts are resistant to moisture absorption and swelling. They are impervious to insects and many chemicals. Ultraviolet stabilizers can be added for outdoor applications.

INSULATING AND DAMPENING

Structural foams are good, sound heat and electrical insulators, significantly better than solid plastic or metal. This makes them especially useful in communications and electronics applications, and in shelters as well as in permanent buildings.

RECYCLING OF RAW MATERIALS

Once a given structure fabricated from a thermoplastic polymer has been damaged or otherwise made not fit for continued use, it can be reground and recycled through another foaming process to make another similar or completely unrelated structure. This would be especially advantageous for items such as pallets that undergo rough handling and are large enough to make recycling of the raw material economical.

DESIGN LIMITATIONS

Generally any piece that can be injection molded can be molded from structural foam. There are some limitations, however. The minimum thickness attainable in structural foam is 4-5mm as structures thinner than this will be nearly solid, thereby losing the specific strength advantage. If the entire finished part can be cooled properly (e.g., by water submersion), there appears to be no limit to the maximum thickness. For example, bowling pins (maximum diameter of 125mm) have been molded from structural foams. Because of the cellular core, structural foams are not generally recommended for use in tension.

APPLICATIONS

HIGH PERFORMANCE FOAM APPLICATIONS

Fuel cells on military aircraft (A-10, F-15, UTTAS and AAH) are currently encased in foam for incendiary ballistic protection. Foams with flammability and insulation characteristics are particularly desirable in submarine application and are being tested on board submarines. Other studies show the effectiveness of foams as laser hardened materials. Also, foams have been adapted for use in defeating tactical mine fields.

LOW PERFORMANCE FOAM APPLICATIONS

Areas currently under investigation are business machine cabinetry, display racks, furniture, tubs, waste receptacles, pallets, containerization for electronic components and ammunition, lightweight gears, tool boxes and vehicle structures.

FOAMS

Practically all thermosetting or thermosetting or thermoplastic resins can be foamed. The decision to use one foam instead of another is generally based on the economics, service temperature, structural load bearing, fabrication and installation techniques as well as specific end use. Foams may contain reinforcements (glass, Kevlar or graphite) if added strength and rigidity are required. Foaming alters the properties of the parent solid polymer as a function of the density achieved, all other factors being equal. Any improvement in the rheological-mechanical properties of the solid polymer would be observable in the foam. Accordingly, molecular and rheological characterization of the polymer to be foamed should be determined as well as the properties special to the use of foams. Examples of several currently used foams are cited and discussed below.

THERMOSETTING POLYURETHANE

The bulk of industrial and other R&D has been done on low density polyurethane foams. Some interesting points noted below pertain to those materials.

TEST METHODS

Tests on raw materials generally tend to be based on classical chemical analysis. These are exemplified in two ASTM standards: ASTM D-1638-70, Urethane Foam Isocyanate Raw Materials; and ASTM D-2849-69, Urethane Foam Polyol Raw Materials. For the foamed material, there are many test methods (listed in Table 1) in use. Physical tests are more widely used than service tests. Many of these correlate well with service performance. However, service requirements generally have not been as stringent as those that would be stipulated in DoD and NASA applications, e.g., sag factor is important in cushioning for chair seats, and is well gaged by an ASTM ILD (Indentation Load Deflection) test.

CELL SIZE, SHAPE, AND MORPHOLOGY

The cell size, shape and morphology have great influence on physical properties. Cell size is often controlled by surfactants. Generally, two catalyst systems are used to produce the structural foam--one builds the polymer while the other builds the foam. At times, three catalysts may be used. There is a delicate balance between these, and the balance governs whether the cells are open or closed. Depending on foaming process and geometry, cells can be highly anisotropic (with smaller cell size, there is less anisotropy). Cell sizes can be quite uniform (governed by surfactant). Varying gradients (e.g., skins) can be generated by altering cooling temperatures.

THERMAL CONDUCTIVITY

The thermal conductivity of foams varies with cell size (in rigid foams), the gas employed in foaming, whether the structure is open or closed, and a number of other factors which interrelate in complicated ways. The following data is for low (1.3 to 8 lb/ft.^{3}) density rigid polyurethane foams.

Thermal Conductivity, K	Blowing Gas
0.21 to 0.29 BTU/sq.ft./hr./°F/in. (at 70°F)*	CO_2 (many interconnecting cells)
0.11 to 0.21 " " " " " " " " "	$CFCl_3$ (closed cells)

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*Per ASTM D 2326, Reference: Modern Plastics Encyclopedia

URETHANE MODIFIED POLYISOCYANURATES

Urethane modified polyisocyanurate foam plastics are now used in the construction market. The increasing awareness of the smoke and toxicity of products of combustion resulting from fire-retarded polyurethanes containing chlorine/phosphorus are promoting the polyisocyanurate technology.

FLAMMABILITY

The flammability characteristics of polyurethane foams as well as other cellular plastic products used in the construction of structures or furniture is being questioned by the Federal Trade Commission. A proposed rule will require marketers and certifiers of cellular plastic products to describe the combustion characteristics of these products to reflect their performance under actual fire conditions.

CROSSLINKING

The degree of crosslinking strongly affects mechanical properties and dimensional stability as well as solvent characteristics.

Table 1 shows the trends (general guidelines in foam R&D) in low density urethane properties with influencing factors. The use of other reactants and modification of both molecular and foam structures produces products with different properties that have been useful in different applications. A summary of various structure-property relationships in rigid urethane foams is presented in Tables 2, 3, 4, and 5. The physical structure and hence the properties of rigid urethan foams varies with the application technique, mainly because of cell size and orientation effects. Some of the more important differences are listed in Table 6. Table 9 shows trends in high density urethane properties with influencing factors.

THERMOPLASTICS - POLYCARBONATE AND POLYETHYLENE

Limited industrial and Department of Defense R&D has been done on structural polycarbonate and polyethylene foams. Test methods for these materials are cited below.

TEST METHODS

In the case of the raw materials, the following methods are employed: ASTM D-1238, Melt Index; ASTM D-1248, Density; and Molecular Weight Distribution (Propriatory). The foamed materials physical tests listed in Table 1 are also used.

Tables 7 and 8 show some properties influencing factors relationship trends for the materials formed by the low pressure injection system technique employing either nitrogen or chemical blowing agents. The most single important factor in structural foam processing is temperature control for product reliability.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The state of the art with respect to structure foams permits one to develop lighter weight but still functional items out of structural foams. This has been made possible by exploratory use studies in which it was found that all of the properties available in a solid material are not essential to the use of many common commercial items.

Commercial success of applications of structural foams has led to the generation of considerable property data for structural foams. Design theories, again following practical exploitation of a material, should lead to even more efficient use of materials and greater reliability of an item.

RECOMMENDATIONS

Continue to exploit the advantages apparent in structural foams in practical applications.

Continue to obtain engineering data on the structural foams used in development programs.

Develop design theory to enable one to design with even greater use to weight efficiency and reliability, e.g., a 75 pound foamed polycarbonate roof panel for the 1976 Model CJ-7 Jeep.

TABLE I Trends in Thermosetting Low Density Rigid Urethane Foam Properties with Influencing Factors[a]

Properties[b] / Influencing Factor	Compressive Strength ASTM-D-1621-64	Flexural Strength ASTM D 790-70	Flexural Modulus ASTM D 790-70	Energy Absorption	Dimensional Stability: ASTM-D-2126-66		Creep ASTM D 2221-68	K-Factor ASTM-D-2326-70	Thermo-Stability (TGA)	Combust-ibility ASTM-D-1692-68	Smoke Evolution ASTM-D-2843-70	Porosity ASTM D-2856-70	Friability ASTM-D-421
					Dry	Humid							
Density ↑	↑	↑	↑	↑	↑	↑	↓	↑	–	(↓)	(↓)	–	↓
Temperature ↑	↓	↓	↓	↓	(↓)	↓	↑	↑	(↓)	↑	–	–	(↓)
Equivalent Ratio (NCO/OH) X 100 ↑	105 ↑ 80	(↑)	(↑)	(↑)	↑	↑	↓	–	↑	↓	↓	–	↑
Hydroxyl Number of Polyol ↑	(↑)	(↑)	(↑)	(↑)	↑	↑	↓	=	↑	(↓)	(↓)	–	↑
Crosslinking Density ↑	(↑)	(↑)	(↑)	↑	↑	↑	↓	–	↑	↓	(↓)	–	↑
Chain Flexibility ↑	↓	↓	↓	↓	↓	↓	↑	–	(↓)	↑	(↑)	–	↓
Cell Structure Fine ↑ Coarse	↑	–	–	↑	↑	↑		↓	–	(↓)	–	↓	↓
% Halogens (Cl & Br) ↑	–			–	–	–		–	–	↓	↑	–	–
% Phosphorus ↑	–			–	(↓)	(↓)		–	↓	↓	↑	–	–

a-University of Detroit and Mobay Chemical Data

b-Rating Key: ↑, increase; (↑), some increase; –, no change; ↓, decrease; (↓), some decrease; blank, no available data.

TABLE 2 Trends in Rigid-Urethane-Foam Properties with Type of Resin Component[a,b]

	Polyol or nonreactive ingredient			
Property	Polyethers	Polyesters	Castor oil	Flame retardants
Mechanical strength	+	+	–	––
Environmental stability:				
Oxidative	–	+	–	=
Hydrolytic	+	–	+	=
Solvent swelling	=	+	–	=
Thermal softening	=	+	–	–
Dimensional stability	+	+	–	–
Thermal conductivity	=	=	=	=
Flame resistance	–	=	–	++
Ease of application	+	–	=	=

[a] Rating key: ++, property greatly improved; +, property improved; =, no effect; –, property degraded; ––, property greatly degraded.
[b] Mobay Chemical Data

TABLE 3 Trend in Rigid-Urethane-Foam Properties with Type of Isocyanate Component[a,b]

	Polyisocyanate		
Property	Distilled TDI	Crude TDI	Polymeric MDI
Mechanical strength	=	=	+
Environmental stability:			
Oxidative	=	=	=
Hydrolytic	=	=	=
Solvent swelling	=	=	+
Thermal softening	–	=	+
Dimensional stability	–	=	+
Thermal conductivity	=	=	=
Flame resistance	–	=	+
Ease of application	–	–	++

[a] Rating key: ++, property greatly improved; +, property improved; =, no effect; –, property degraded.
[b] Mobay Chemical Data

TABLE 4 Trends in Rigid-Urethane-Foam Properties with Type of Blowing Agent and Cell Structure[a,c]

	Blowing agent		Cell structure	
Property	$CFCL_3$	[b] CO_2	Open	Closed
Mechanical strength	=	+	=	=
Environmental stability:				
Oxidative	=	=	=	=
Hydrolytic	=	=	=	=
Solvent swelling	=	=	=	=
Thermal softening	=	+	=	=
Dimensional stability	–	+	++	–
Thermal conductivity	++	=	=	+
Flame resistance	=	=	=	=
Ease of application	+	–	–	+

[a] Rating key: ++, property greatly improved; +, property improved; =, no effect; –, property degraded.
[b] Produced by the reaction between isocyanate and water.
[c] Mobay Chemical Data

TABLE 5 Trends in Rigid-Urethane-Foam Properties with Increasing Concentrations of Structural Elements Introduced in Reactive Components[a,c]

		Aliphatic structure			Alicyclic or aromatic structure	
Property	Crosslink density	Ether	Ester	Hydrocarbon	Single ring	Multi-ring
Mechanical strength	–	–	–	–	+	++
Friability	–	+	–	+	–	––
Environmental stability:						
Oxidative	–	–	=	–	+	+
Hydrolytic	–	+	–	+	+	+
Solvent swelling	–	–	=	–	+	++
Thermal softening	–	–	–	–	+	++
Dimensional stability	–	–	–	–	+	++
Water-vapor permeability	–	–	–	+	+	+
Thermal conductivity	=	=	=	=	=	=
Flame resistance	=	––	–	–	=	++
Ease of application	=[b]	+	=	+	=	–

[a] Rating key: ++, property greatly improved; +, property improved; =, no effect; –, property degraded; ––, property greatly degraded.

[b] Best processing occurs at an optimum crosslink density.

[c] Mobay Chemical Data

TABLE 6 General Characteristics of Rigid-Urethane-Foam Application Methods[a]

	Method of application			
Characteristic	Slab	Spray	Molding	Froth molding
Foam properties isotropic	Can be	Highly oriented	Oriented	Oriented
Foam internally stressed	Slightly	Highly	Yes	Yes
Maximum temperature of exotherm	High	Low	Moderate	Moderate
Pressure exerted	Expansion not restricted	Expansion not restricted	Relatively high in closed molding	Lower than normal molding
Ease of application:				
As sheets	Good	Poor	Poor	Poor
Over odd surfaces	Poor	Good	Good	Good
In complex shapes	Poor	Poor	Good	Good
In-plant	Good	Moderate	Good	Good
Field operation	Poor	Good	Moderate	Moderate
Machine expense	High	Low	Moderate	Moderate

[a] Mobay Chemical Data

TABLE 7 Trends in Thermoplastic High Density Polycarbonate Structural Foam Properties with Influencing Factors[a]

Properties[b] / Influencing Factor		Tensile Strength	Compressive Strength	Flexural Modulus	Flexural Strength	Energy Absorption	Dimensional Stability:		Creep	K-Factor	Thermo-Stability	Combust-ibility	Smoke evolution
							Dry	Humid					
Density wall Sp. G. .8-1.0 @ R.T., ¼"	↑	(5100- ↑ 6200 PSI)	↑	(325×10^3- 368×10^3 PSI) ↑	↑	↓	-	-	↓	(↑)	-	(↓)	(↓)
Temperature ¼" wall (80°-240°F)	↑	(5100- ↓ 3000 PSI)	↓	(325×10^3- 235×10^3 PSI) ↓	↓	↑	-	-	↑		↓	-	-
MW Distribution Narrow ↑ Broad		-	-	-	-	↑	-	-	-	-	-	-	-
Wall Thickness	↑	↓	↑	-	↓	(↑)	-	-	(↑)	-	-	-	-
Processing Conditions:													
Melt Temperature 550 ± 20°F		-	-	-	-	-	-	-	-	-	-	-	-
Mold Temperature (180 ± 20°F)		-	-	-	-	-	-	-	-	-	-	-	-

a-G.E. Data

b-Rating Key: ↑, increase; (↑), some increase; –, no change; ↓, decrease; (↓), some decrease; blank, no available data.

TABLE 8 Trends in Thermoplastic High Density Polycarbonate Structural Foam Properties with Influencing Factors[a]

Properties[b] / Influencing Factor		Tensile Strength	Compressive Strength	Flexural Modulus	Flexural Strength	Energy Absorption	Dimensional Stability: Dry	Dimensional Stability: Humid	Creep	K-Factor	Thermo-Stability	Combust-ibility	Smoke evolution
Density (0.6 to solid g/cc @ R.T., ¼" wall)	↑	(1300- ↑ 4000PSI)	(1000-↑ 3600 PSI)	(2700- ↑ 5000 PSI)	(120 x 10^3 160 x 10^3 PSI) ↑		–	–	(↓)	↑	–	(↓)	
Temperature	↑	↓	↓	↓	↓		–	–	↑	↑	↓		
MW Distribution Narrow · Broad	↑	(↑)	–	(↑)	(↑)		–	–	(↓)		–	–	
Wall Thickness	↑	(↑)	↑	↑	(↑)		–	–	(↓)				
Processing Conditions: Melt Temperature (500 ± 5°F)		–	–	–	–								
Mold Temperature (45±5°F)		–	–	–	–								

a-Union Carbide Data

b-Rating Key: ↑, increase; (↑), some increase; –, no change; ↓, decrease; (↓), some decrease; blank, no available data.

TABLE 9 Trends in Thermosetting High Density Urethane Structural Foam Properties with Influencing Factors[a]

Properties[b] / Influencing Factor		Flexural Modulus	Flexural Strength	Compressive Strength	Tensile Strength	K-Factor	Surface Hardness	Heat Distortion Temperature	Charpy Impact
Density	↑	↑	↑	↑	↑	↓	↑	↑	↑
Mold Temperature	↑	↓	(↓)		(↓)	-	↓	↓	↓
Equivalent Ratio (NCO/OH) x 100	↑	(↑)	(↑)	(↑)	(↑)	-	(↑)	(↑)	(↑)
Resin OH # Crosslinking Density	↑	↑	↑	↑	↑		-	↑	↑
Part Thickness	↑	↓	(↑)	↑	↑		-	↑	↑

a-Mobay Chemical Data

b-Rating Key: ↑, increase; (↑), some increase; –, no change; ↓, decrease; (↓) some decrease; blank, no available data

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