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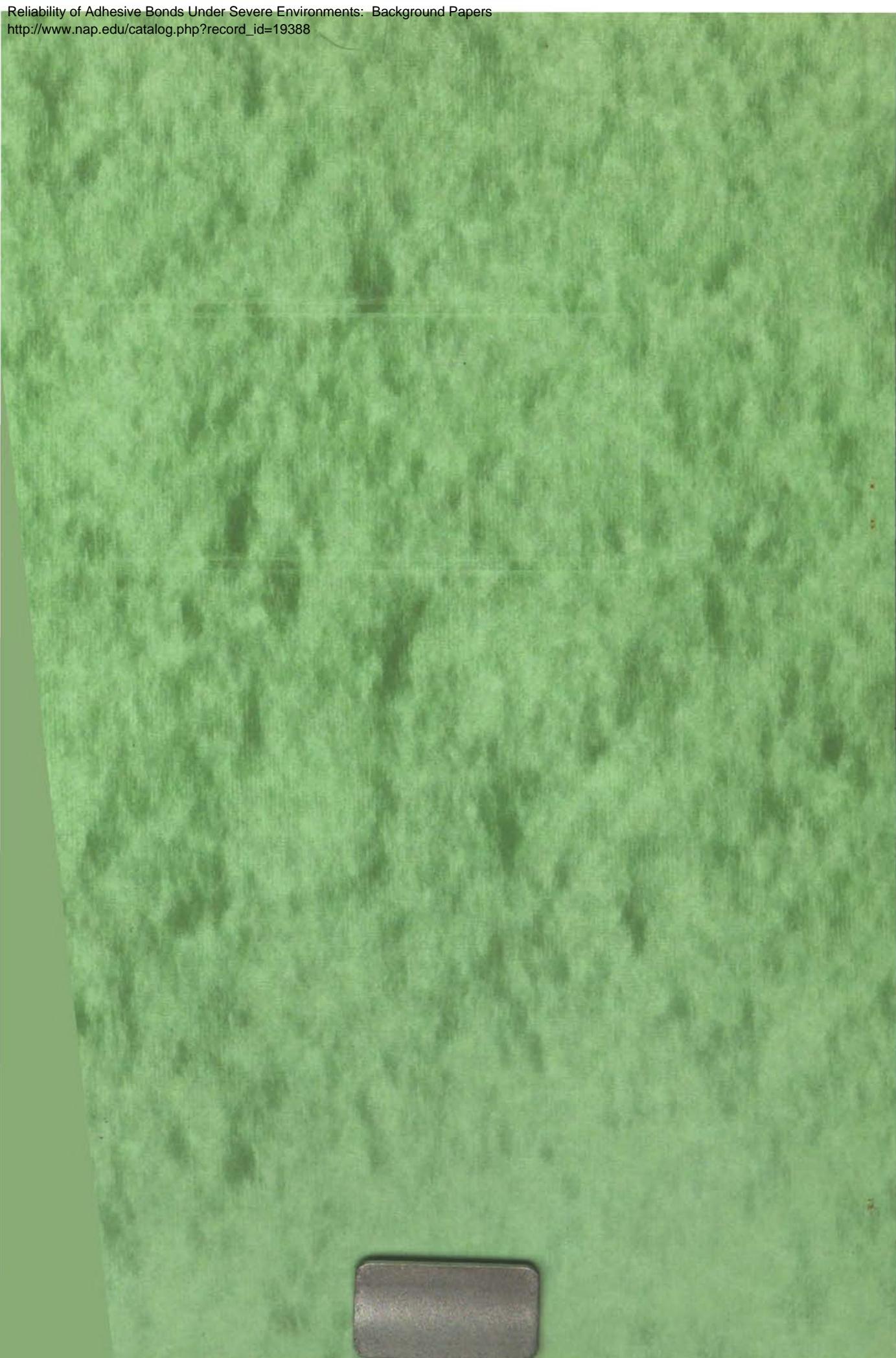🔍 **Find Similar Titles**   ▤ **More Information**

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RELIABILITY OF ADHESIVE BONDS
UNDER SEVERE ENVIRONMENTS

Background Papers

National Materials Advisory Board
Commission on Engineering and Technical Systems
National Research Council

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17 May 1984

REC'D
MAY 21 1984

Joseph R. Lane
National Research Council
Commission on Engineering and Technical Systems
2101 Constitution Avenue
Washington, D.C. 20418

Dear Joe:

After sending you the copies of my summary I had a few minutes time on a flight to San Francisco to proof read it. I found a couple of typos and discovered I had left one name out of the credits. Would you please substitute the enclosed copy for the earlier one? I hope this has not inconvenienced you. Please call on me if I can assist further.

Best wishes,

K. L. DeVries

/jro

ADHESIVE MECHANICS

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The following is a brief snyopsis of my presentation at the National Material Advisory Board Workshop on the Reliability of Adhesive Bonds under Severe Environments. Due to space limitations it contains no figures or references. More details are included in the original report, copies of which can be obtained from the author.

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

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

There has been no dearth of methods proposed and developed to explore adhesives. Some of these have been formalized and published as standards (e.g., by governmental agencies, ASTM, etc.). Except for a few notable exceptions these suffer from a common problem and hence can be used to predict performance only for practical joints that very nearly duplicate the test specimen's exact geometry. That is, in most standard tests, little if any attention is given to the details of the stress distribution in a joint, rather, results are almost universally given as gross force per unit area. Therefore, these tests yield little if any information on extreme values of the stress or point of failure initiation. There is evidence that the reported "average stresses" may have little direct bearing on the actual failure. One of the most common and useful type of adhesive test is the single-lap shear test. Not only is it simple and economical to conduct but superfically it closely resembles the type of loading to which structural adhesives are often subjected in service. Care must be exercised, however, in interpreting the results and trying to infer strength of practical joints from the given test results. For example, the results of these tests are conventionally given as failure load divided by the area of overlap. Computer analysis shows that the actual stress is far from uniform and becomes much larger than this reported average near the ends of the overlap. For linearly elastic materials, it is mathematically singular. Perhaps more significantly, the loading of the lap shear joint induces tensile stresses that again become very large near the terminus of overlap. The relative value of the shear and normal stresses depends on details of the adhesive and adherend properties, thicknesses, etc. These tensile stresses are particularly acute for comparatively thin adherends (as generally used in ASTM tests). The evidence is very strong that failure of the joint is more closely related to these crack opening cleavage stresses than to the shear stresses (let alone the

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

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

A few observations on adhesive fracture mechanics might be helpful. Inherent in the concepts of fracture mechanics is the concept that cracks are likely to initiate at flaws or discontinuities. In the case of bonds additional elastically singular regions can occur at points of abrupt changes in section, geometry modulus, etc. While superficially several FM approaches appear different in concept, such approaches as the energy release rate, the stress intensity factor and J integral can be shown to be essentially equivalent (at least in the elastic case). Considerable evidence exists that adhesive failure is highly dependent on the exact mode of stress at the crack (debond) tip. Modern computational methods, particularly finite element techniques, have greatly expanded the potential of FM and the geometries, joints, etc., for which it might be used. There is a wealth of FM data, methods, experimental techniques, etc., available upon which to base future studies of durability adhesives in severe environments. Techniques have been developed to study both static failure ($G_{I,II,III}$) and fatigue crack growth.

Tests are needed to determine the critical value of the energy release rate G_c, the critical stress intensity factor K_c or the critical value of the J integral J_c (perhaps for each of the loading modes). In principle almost any test could be used. Certain techniques, however, enjoy certain experimental and analytical advantages. A. N. Gent, G. R. Hamed et al. have made extensive and fruitful use of peel tests to analyze a wide variety of different fracture mechanical aspects of adhesives. Likewise the blister test proposed by M. L. Williams has been adopted by W. B. Jones, G. P. Anderson, B. J. Bennett, K. L. DeVries, and others to measure G_c for a variety of different adhesive systems. A tapered double cantilever beam developed by E. J. Ripling and S. Mostovoy and used by them, W. Bascom and others forms the basis of the comparatively new testing standard (ASTM D3433). W. S. Johnson and his associates at NASA have been testing and analyzing a variety of different geometries as adhesive fracture mechanics test specimens. It is important to recognize that many other experimental geometries could be used. Fracture mechanics should not be envisioned as a set of rules and/or sample configurations for testing and design. Rather it should be thought of more as a basic philosophy and methodology for approaching testing, design and evaluation. It may at times be expedient to tailor-make tests for a given system or to design adhesive joints that do not closely resemble the adhesive test in which the adhesive was originally evaluated. In problems of these types, fracture mechanics has inherent potential advantages over other available approaches.

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

It is a priori that it would be advantageous to have non-destructive methods of detecting flaws such as cracks or regions of debond along the bond line. The optimal NDE test would be one in which a measurement could be quickly and easily made that does not damage the joint(s) or structure and yields results that can be directly related to the strength of the bond. A great many experimental techniques have been brought to bear on this problem including: 1) For adherend surface inspection, (a) contact angle, (b) surface potential difference, (c) surface impedance; 2) For NDE of the complete bond, (a) capacitance measurement, (b) radiographic (X-ray, γ-ray, neutron, etc.), (c) thermal inspection methods including variations in thermal conductivity, thermal emissivity, thermal capacity or local differences in thermal expansion, (d) acoustic emission (similar to that previously described), (e) acoustic inspection such as the coin tap and its related instrumental counterparts such as the Fokker Bond Tester Type I, (f) ultrasonic techniques including through transmission, pulse echo techniques, resonance techniques and spectral analysis, (g) acoustic emission, and (h) holographic interference.

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

Acoustic emission (AE) shows promise of providing a measure of the "onset" and "accumulation" of damage. G. P. Anderson of Morton Thiokol reports, for example, that in studies of debonding of a system tunnel that runs the entire length of the space shuttle AE techniques readily detect damage at loads of 40 to 60% of those for which there is any visual evidence of damage.

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

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

Information provided by G. P. Anderson, W. Bascom, H. Brinson, B. Djordjevic, A. N. Gent, G. R. Hamed, W. S. Johnson, W. Knauss, S. Mostovoy, E. S. Ripling and William B. Jones was invaluable in preparing the presentation at the workshop and this synopsis.

RECENT DEVELOPMENTS IN ADHESIVE

AND SEALANT CHEMISTRY

by

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To be presented to:

Virginia Polytechnic Institute and State University (5-2-84)
NMAB-NRC at the East Room of the State Department (5-3-84)
International Adhesion Conference, Nottingham, England (9-12-84)

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I. INTRODUCTION

The use of synthetic adhesives in the past twenty-five years (1) has grown, particularly the use of eight classes of polymers: polyvinyl acetate, polyolefins, styrenic block copolymers, acrylics, cyanoacrylates, aneorobics, polyurethanes, and epoxy resins. Some of these polymers are still in high demand as specialty adhesives (2). During the last several years, however, other polymers have been added to this list, e.g., polyamides, polyimides, and polyesters. Today, synthetic adhesives account for 75% of the adhesives produced and 85% of the sales, while the market share of natural products has steadily declined.

The growth in the use of structural adhesives (3) will remain at 3-4% a year throughout the 1980's. The use of new "high-technology" structural adhesives, especially for the aerospace industry, may increase at a higher rate in light of the new developments discussed in this paper. For example, recent applications of robotics could enhance the large-volume use of adhesives for primary-bonded structures in aircraft. Thus, along with other recent developments, the share of the fastening and joining materials market attributed to adhesives could increase from 22% in the 1970's to 35% in the 1980's.

In this paper, we shall describe the development of adhesives during the last several years and the trends for further advances. In general, traditionally used, solvent-borne systems (4) will be gradually replaced by waterborne systems, hot-melts, nonvolatile solid (or liquid) systems, two-part adhesives, radiation-curable adhesives, and powder and reactive liquid systems (Table 1).

In the following sections, we shall discuss: adhesion chemistry, adhesion physics, radiation-curable adhesives, high-temperature adhesives, anaerobic and structural adhesives, hot-melt adhesives, film adhesives, waterborne adhesives, aerospace structural adhesives, conventional sealants, advanced aerospace sealants, and adhesives and sealants for solar collectors.

Table 1. Growth Market Technology Profile*

System	Number of Growth Opportunities
Water-borne	56
Hot-melts	36
Non-volatile solid or liquid	14
Two-part	10
Radiation-cured	5
Reactive-liquid	2
Powder	2
Solvent-borne	0
Total	$\overline{125}$

* Data from the paper by H. Ellerhorst, Jr., Adhesives Age, 25, 42 (1982).

II. CHEMISTRY OF ADHESION - THE IMPORTANCE OF INTERFACE

Since my last review of adhesion chemistry (5) several books have been published on this subject (6-9) and Kinloch has written two reviews that cover both the surface chemistry (10) and the mechanics of adhesive joints (11). Despite the progress made in fracture mechanics, basic surface chemical interactions still govern adhesion at the monolayer level. Without these, the joint has no foundation. For example, it has been established (12) that the threshold failure energy θ_o approaches the thermodynamic work of adhesion W_A. Recently, surface energetics have been related to fracture surface energetics of polymers (13,14). A new interpretation of the surface energies of polymers will be described by Lee (15).

The importance of surface modification to adhesion has been recognised by many authors. A microwave plasma treatment (16) has been used to modify the acid-base balance

*Registered trademark of DuPont Company.

of the polymer-filler surface. Reactive groups such as isocyanate, acyl chloride, and azo (17) have been introduced onto polymer surfaces to modify surface properties and adhesion. The surface of Kevlar Ⓡ has been modified (18) to provide reactive amine sites for enhancing its adhesion to an epoxy resin and the water sensitivity of many polymer surfaces can be reduced by plasma polymerization (19). These are only a few examples of how surface modification can influence adhesion. The characterization of these modified surfaces requires the use of new techniques (20) such as ESCA, to be discussed in the following section.

III. PHYSICS OF ADHESION - THE CHARACTERIZATION OF SURFACE AND BULK

Adhesion may not be regarded just as a phenomenon related to the contact of two solid bodies. Recently, physicists have applied the concept of adhesion to understand the structure of basic particles at the subatomic level (21). New terms, such as "glue balls" or "gluons," have appeared in particle and nuclear physics literature. The phenomena of adherence have been studied by Maugis and Barquin (22) and Maugis (23).

New instrumental surface techniques (24) have been introduced to study adhesion during the last ten years. Among them, ESCA (or electron spectroscopy for chemical analysis) techniques (25) have given us insights about the structure of the polymeric interface within the first 50Å. New applications of ESCA are discussed by Briggs (26). A combination of ESCA and AES (27) has been used to investigate the interfacial bonding between aluminum and chromium(III) fumarato-coordination compounds.

Not only new techniques deserve attention, but also any new developments in old techniques, such as electron scanning microscopy (28). Electron scanning microscopy, for example, can now enhance the examination of the adhesive interface in greater detail. Two other old techniques have also found new applications in adhesive chemistry. One is dynamic mechanical analysis (29,30), which has been accepted for the study of pressure-sensitive adhesives and the curing mechanism of epoxy resins (31,32). The other is the use of a fluorescence probe to examine the curing mechanism (33).

An exciting contribution by Dickinson (34) is the application of fractoemission in studying the phenomena of adhesive failure. The emission of electrons (EE) and positive ions (PIE), as well as free radicals, has been vividly shown during the fracture processes. In addition, the energetics distribution of the emission can be accurately measured.

IV. RADIATION-CURABLE ADHESIVES

The contributions of physics to adhesion are further manifested by the extension of uv- and electron-beam curing of adhesives to low temperatures. Radiation-curable adhesives were originally intended to eliminate solvents in the systems. However, the use of certain toxic acrylate monomers presented some problems. So far, radiation-curable systems have become technologically challenging, but economically less attractive than most thermally cured systems. Since one of the earliest papers on photo-adhesives by Nakano (35) many patents have been issued on this subject. Two reviews have been published by Stueben (36).

Free-radical, radiation-curable systems generally consist of monomers, oligomers, photoactivators, other resins, and fillers or tackifiers. An ultraviolet source or electron-beam generator is used to cure the systems. As an illustration Stueben (37) describes a typical uv-cured PSA system containing acrylates and polyvinyl ether. McGinniss (38) discusses formulation design related to uv-curable systems. The cationic photoinitiators are shown in Fig. 1.

where MX_n^- is BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, ClO_4^-, etc.

Fig. 1. Photoinitiators for Cationic Polymerization

(Ref: J. V. Crivello and H. W. Lam, J. Polym. Sci., Polym. Chem. 18, 2677 (1980).)

Ledwith (40) has recently discussed his new findings related to the polymerization mechanisms involving cation radicals (Fig. 2). By the same type of polymerization, the addition of acrylate to epoxide (41) created a product superior to that derived from epoxide or acrylate alone. The radicals generated during the cationic polymerization are presumably used for grafting acrylate onto the epoxide (42).
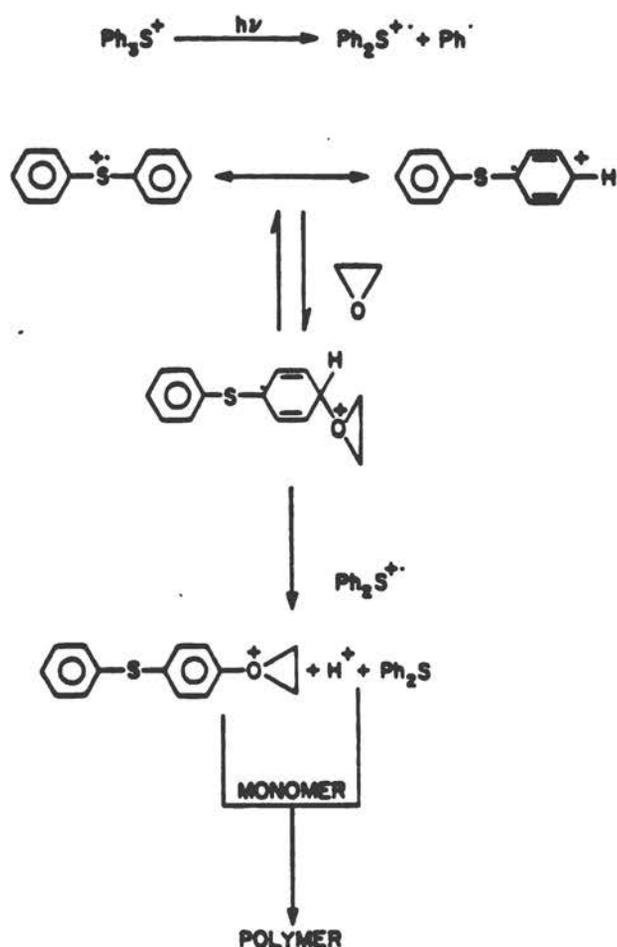

Fig. 2.   Cation-radical Mechanism for Photopolymerization

(Ref: A. Ledwith, a paper presented to the Northeast
        Regional ACS Meeting, Rochester, N.Y., Oct. 1981.)

In fact, the importance of the cationic photo-
polymerization lies beyond epoxides (39). Many oxygen-
containing compounds, e.g., vinyl ethers, tetra-
hydrofuran, oxetane, lactones, trioxane, and some un-
saturated compounds (Fig. 3) can be polymerized by the same
mechanism to form adhesives or coating materials. Crivello
(43) reviews the scope of cationic photopolymerization,
providing us with a perspective on this promising process.
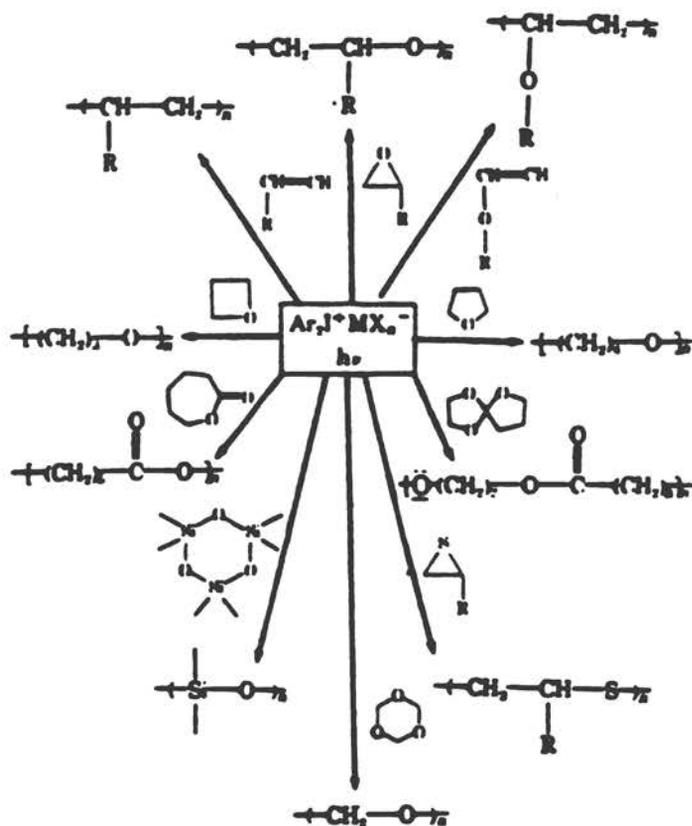

Fig. 3.   Photoinitiated Cationic Polymerization using
          Diaryliodonium Salt

(Ref: J. V. Crivello, CHEMTECH, 10, 624 (1980).)

In recent years, not only has uv-curing been accepted by the adhesive industry, but electron-beam (E-B) curing is also being applied to continuous operation (44). E-B curing uses low energy electrons (<300 kV) generated from a filament, as shown in Fig. 4. The electrons are then accelerated in a field of 100-300 kV before hitting a target on a moving web, which is only 1 to 2 inches from the window. Since electrons move at a very high velocity, very little energy is lost when they move through the window.

The depth of electron penetration depends on the density of the material. Thus, the penetration ability of the processor is quoted as thickness of unit density product or weight per unit area, e.g., gram per square meter or pound per ream (1 lb/ream=1.6 g/m^2). The relationship between the electron dose (% front surface) versus penetration is shown in Fig. 5. The only way to increase the penetration depth is to increase the accelerating voltage.

For EB curing, the important processing parameters are the beam current I_e, the voltage V_e, and the product speed S. E-B processor performance is characterized by the yield factor (k), which relates I_e, V_e, and S through the dosage, D:

$$D = \frac{k \cdot I_e}{S} \tag{1}$$

The units of the parameters are mrads for D, mA for I_e, and ft/min for S. At a given preset dosage, line speed is the primary process parameter in a slave mode of operation.

The advantage of E-B is its high-speed curing of adhesives on paper, film, foil, fabric, and other flexible substrates. For E-B-cured, hot-melt adhesives, the modulus, plasticity, creep, tack, etc., can be controlled in situ. Though the capital investment is high, a cost advantage can be realized for a large-volume, high-speed curing operation.
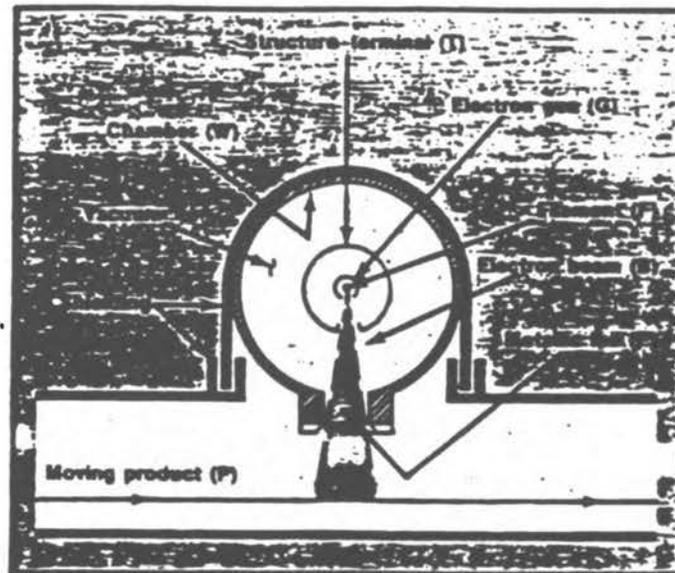
Fig. 4. Schematic of Electron Processor

(Ref: R. Kardashian and S. V. Nablo, Adhesives Age, <u>25</u>, No. 12, 25 (1982).)
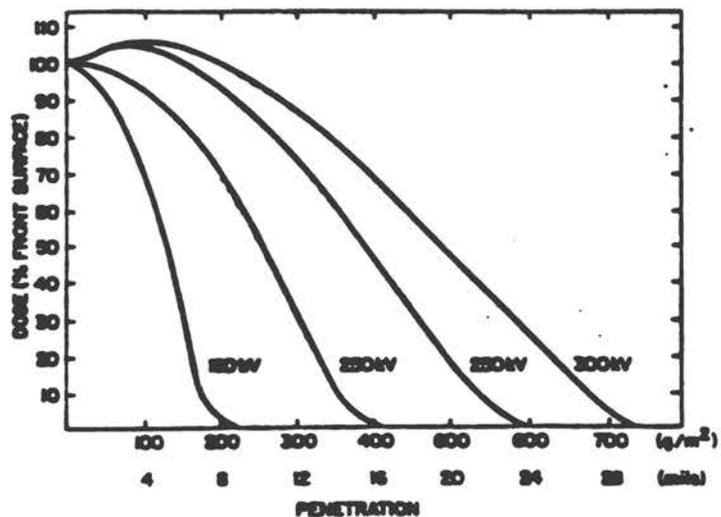

Fig. 5. Processor Penetration Performance in Unit Density Product

(Ref: R. Kardashian and S. V. Nablo, Adhesives Age, <u>25</u>, No. 12, 25 (1982).)

V. HIGH-TEMPERATURE ADHESIVES

The aerospace industry has developed strong demands for high-temperature adhesives. The adhesives used on missiles (45,46) require mechanical performance for less than one minute but at temperatures greater than 538°C (Fig. 6). Thus, organic polymers with exotic structures have been designed to meet such high-temperature requirements (47).

For adhesive applications, thermal stability alone is insufficient. Processability of high-temperature polymers is of great importance. These polymers should be processed under moderate conditions with no volatile evolution. The adhesives should be compatible with adherends and should have good, durable properties. For broader uses, the manufacturing cost should be low because cost, so far, has been the major obstacle to developing high-temperature adhesives.
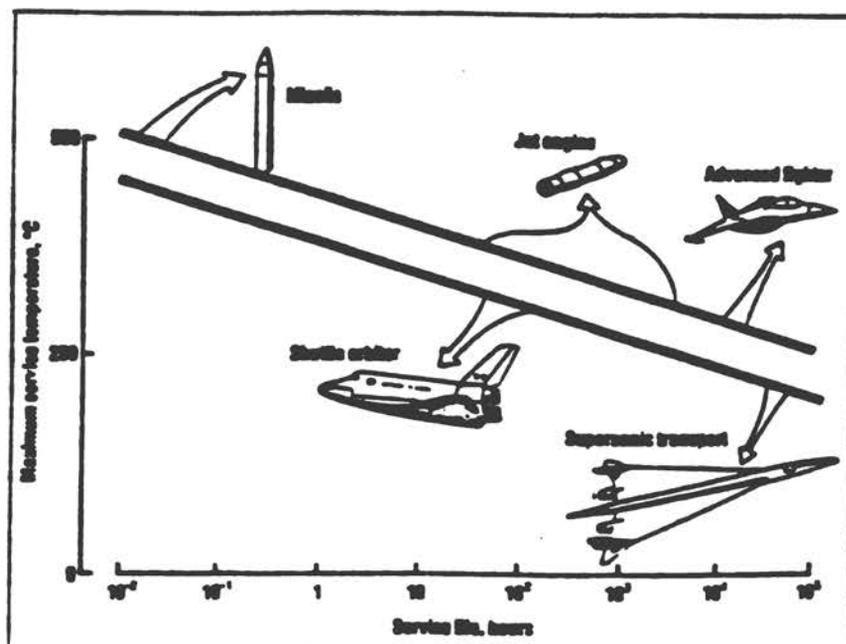

Fig. 6.   Service Lives of High Temperature Adhesives versus Maximum Service Temperatures.

(Ref: A. K. St. Clair, NASA Technical Memorandum 81884, Oct. 1980.)

During the last several years, a thermoplastic condensation polyimide (PI) was developed at NASA Langley Research Center (49). From the reaction between BTDA (3,3', 4,4'-benzophenonetetracarboxylic acid dianhydride) and DABP (3,3'-diamino benzophenone), the polyimide LARC-TPI (Fig. 7) was prepared by Bell et al. (49). Later, St. Clair (50) used LARC-TPI as an adhesive for titanium. The adhesion of titanium and PI has been studied by Wightman et al. (51) with XPS (ESCA) and FT-IR techniques.

Besides the condensation PI, there have been two new types of addition PI's: ethynl (acetylenic) and norbornene (nadic) end-capped PI. The acetylene-terminated PI (ATI) was first reported by Bilow and co-workers (52) and the nadic-terminated PI (NTI) (Fig. 8) was derived from the work of Lubowitz (33). An NTI prepared at NASA Langley Center has been designated as LARC-13 (34). When LARC-13 was compared with ATI as the adhesive for titanium, the lap shear strength of LARC-13 after 1000 hours at 232°C was lower than that of ATI.

Many polyimides are brittle. To toughen a brittle PI, special elastomers (55) have been added. Silastic rubber, vinyl fluorosiloxane, and Sylgard, divinyl-dimethyl-siloxane, can be directly blended with PI, e.g., LARC-13. Two amino-functional elastomers have been used successfully: (1) ATBN, aniline-terminated butadiene-nitrile rubber, and (2) ATS, aniline-terminated di-methylsiloxane.

Polyphenylquinoxalines (PPQ's) were first prepared in 1967 by Hergenrother (56). In 1975, Koval et al. (57,58) introduced the acetylene-terminated PPQ (ATPQ) (Fig. 10), which is the addition type of PPQ. Resembling ATPI, ATPQ also has shortcomings. The ethynl group hinders the flow of the polymer chain, and the cured ATPQ is less thermal-oxidatively stable than the comparable PPQ. The detailed status of PPQ, as well as other high-temperature adhesives, is discussed by Hergenrother (45).

The properties of several typical high-temperature adhesives are listed in Table 2 (59). Note that one listed is FM-34 condensation polyimide from the Bloomingdale Division of American Cyanamid Company. The contributions of the above high-temperature adhesives to the aerospace structural adhesives will be discussed later.
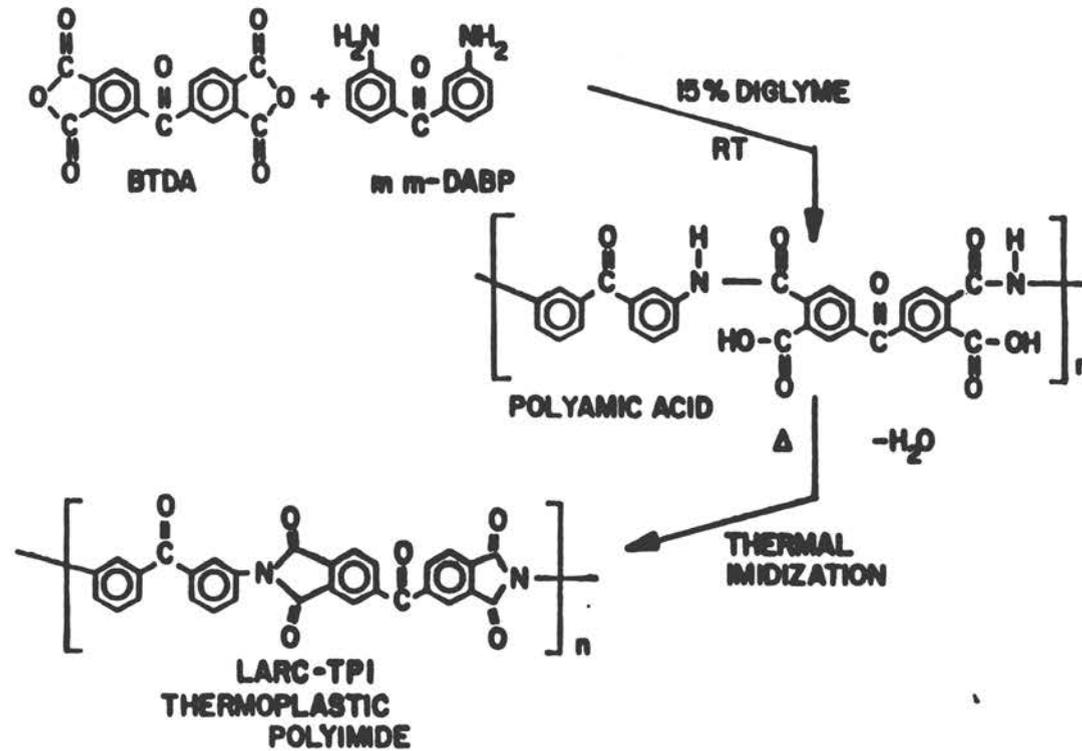
Fig. 7. Preparation of LARC-TPI Adhesive

(Ref: V. L. Bell, B. L. Stump, and H. Gager, J. Polym. Sci.,
Polym. Chem. Ed. 14, 2245 (1976).)
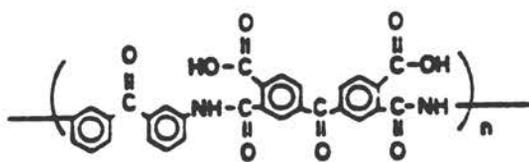
LARC-2 POLYAMIC ACID ADHESIVE
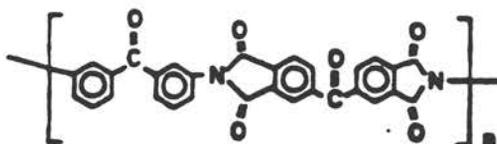
LARC-TPI
THERMOPLASTIC
POLYIMIDE
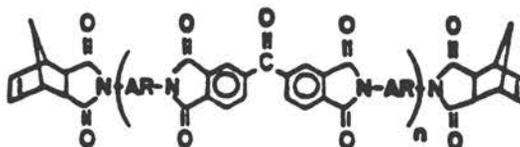
NADIC-TERMINATED IMIDE (NTI)
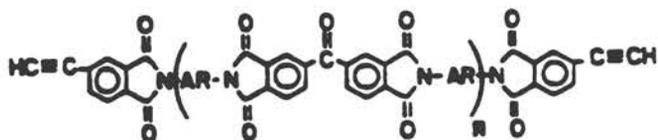
ACETYLENE-TERMINATED IMIDE (ATI)

ATPQ

Ar = φ-O-φ

Fig. 8. Structures of High Temperature Adhesives
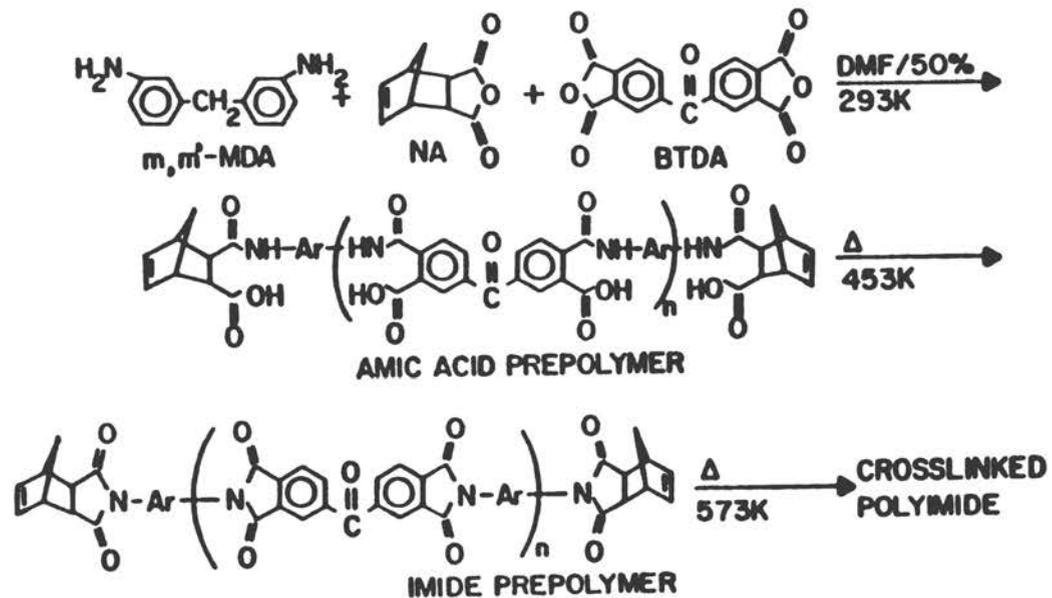
Fig. 9. LARC-13 Adhesive Chemistry

(Ref: A. K. St.Clair and T. L. St.Clair, Polym. Eng. and
       Sci., 22, No. 1, 9, (1982).)
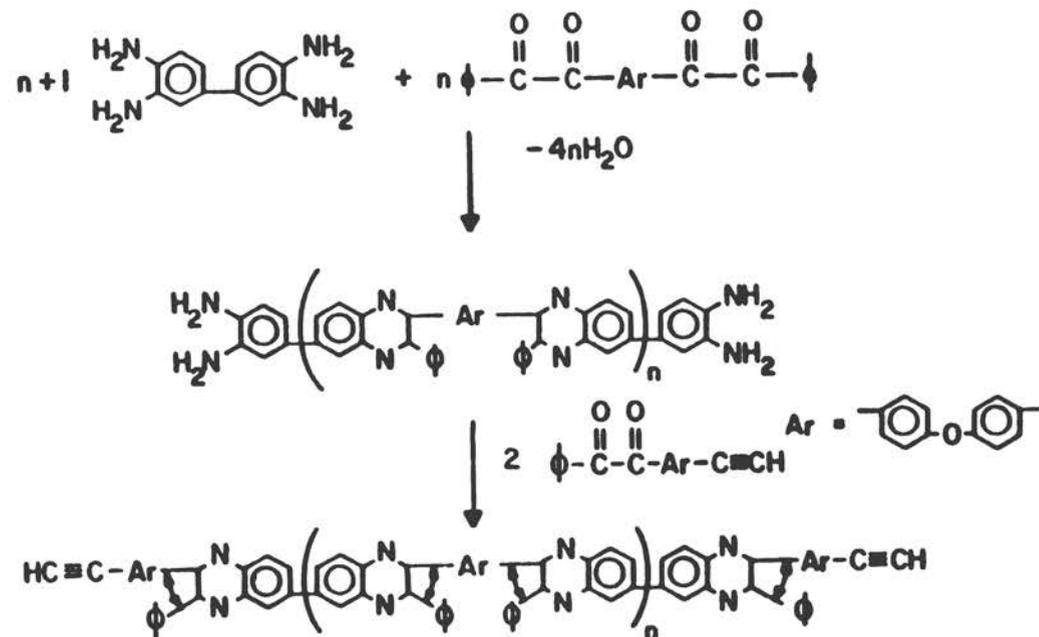
PREPARATION OF ATPQ OLIGOMER

(Ref: P. F. Kovar, G. F. L. Ehlers, and F. E. Arnold, Polym. Chem. Preprints, 16, (2) 246 (1975).)

Table 2. High Temperature Adhesive Tape Properties

Adhesive	PM-34	NR-056X	LARC-13	PPQ
Filler	Yes	Yes	Yes	No
Tack	Yes	No	No	No
Drape	Yes	No	No	No
Flow	Good	Good	Good	Fair
Shelflife	Poor	Poor	Good	Good
Volatiles, %	~14	~11	<1	<1

(Ref: P. M. Hergenrother, "High-temperature Adhesives,"
lecture notes for the course on "Fundamentals of
Adhesion," State University at New Paltz, New York,
Nov. 1983.)

VI. ANAEROBIC AND STRUCTURAL ADHESIVES

Acrylic polymers are one of the important structural
adhesives (Fig. 11). These polymers can be classified as
anaerobic structural acrylics (60), second generation
acrylics (60,61), and aerobic acrylics (61,62). Most
anaerobic adhesives are based on dimethacrylic esters,
e.g., TEGDMA (triethylene glycol dimethacrylate) (Fig.
12). Anaerobic adhesives (63) containing maleimides have
been reported to have improved thermal resistance.

Recently, the curing characteristics of anaerobic
sealants and adhesives (Fig. 13) were reported by Lees (60)
and Stamper (64). The present systems can be cured rapidly
in most metallic substrates, yet possess shelflives in
excess of one year. The factors affecting curing are the:
cure system, surface preparation, substrate, temperature,
and bondline thickness.

Cyanoacrylates (65) are no longer the wonder-glues for
small applications. In general, newer, modified cyano-
acrylates can be used on porous surfaces, oil-contaminated
metals, and even wood. Some recently introduced grades can
have a service temperature as high as 150°C, and are less
sensitive to humidity. Furthermore, impact resistance has
been improved to qualify the adhesives for applications
such as mounting door trims on autos.

CYANOACRYLATE-RAPID BONDING
SMALL SCALE
FOR USE UNDER BENIGN CONDITIONS

UV CURING ADHESIVE- FOR BONDING GLASS TO A VARIETY OF SUBSTRATES

$$CHR_1 = C - C$$

R_2

O

O - X

ANAEROBIC- LOCKING, BONDING SEALING THREADED AND PLANE CO-AXIAL JOINTS. FLANGE SEALING AND THE ADHESION OF SMALL PARTS MAY USUALLY BE USED UNDER HARSH CONDITIONS

TOUGHNED ADHESIVES- PERMANENT BONDING OF SMALL AND LARGE STRUCTURES IN MOST CONFIGURATIONS CAN OFTEN BE USED UNDER HARSH CONDITIONS

Fig. 11. New Developments in Acrylic Adhesives

(Ref: W. A. Lees, Brit. Polym. J., 11, 64 (1979).)

ANAEROBIC ADHESIVES

TEGDMA AND 'HOMOLOGUES' ARE REMARKABLE MOLECULES

$$CH_2=CH-\overset{O}{\overset{||}{C}}-O-\left[CH_2CH_2-O\right]_3\overset{O}{\overset{||}{C}}-CH=CH_2$$
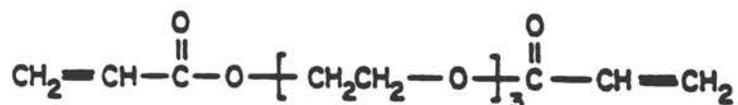
OR FOR THE 'HOMOLOGUES' —

$$Ac-X-R$$

WHERE X IS ANY ESTER-BASED GROUP(S) AND R IS
USUALLY, H, OH OR A FURTHER ACRYLIC ESTER.

Fig. 12. Anaerobic Adhesives

(Ref: W. A. Lees, Brit. Polym. J., 11, 64 (1979).)

The second generation acrylics have also been called
"reactive acrylics", "toughened acrylics," or "modified
acrylics." These adhesives can be bonded rapidly at room
temperature   and   are   somewhat   tolerant   to   an   oil-
contaminated surface. The bonds are flexible and give high
peel and impact strengths. Generally, these adhesives have
good low temperature properties, good heat resistance, and
excellent solvent resistance. For formulation, they have a
long open-time and provide flexibility for specific end-use
requirements. The acrylics approach the tensile-lap shear-
strength level of the epoxies - 4000 psi (28 MPa) 2024-T3
aluminum-to-aluminum for acrylics versus 4,740 to 6,000 psi
(34-41 MPa) for a typical epoxy.

$$T^{1+} + CH_3-\!\!\bigcirc\!\!-N\!\!<^{CH_3}_{CH_3} \rightarrow T^{2+} + CH_3-\!\!\bigcirc\!\!-N\!\!<^{CH_3}_{CH_3} +H^+$$

(₀)

HENCE:

$$RO_2R + T^{2+} \longrightarrow T^{3+} + RO^\circ + RO^-$$

$$T^{3+} + AH \longrightarrow T^{2+} + A^\circ + H^+$$

ADD $RO_2R + T^{2+} + T^{3+} + AH \longrightarrow T^{3+} + RO^\circ + RO^- + T^{2+} + A^\circ + H^+$

SUBTRACT $T^{2+} + T^{3+}$

$$R_2OR + AH \xrightarrow[T^{2+} \rightleftharpoons T^{3+}]{CATALYTIC} RO^\circ + ROH + A^-$$
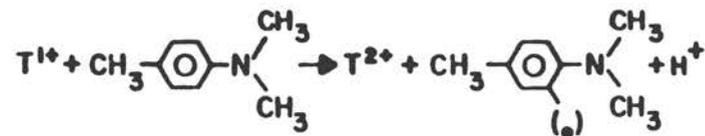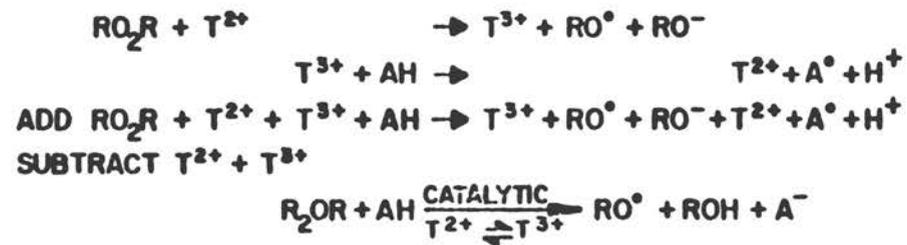
WHERE: T IS A TRANSITION METAL
AH IS THE AMINE
R IS ANY SUITABLE GROUP
A IS A STABLE STRUCTURE

Fig. 13. Curing Mechanism of Anaerobic Adhesives

(Ref: W. A. Lees, Brit. Polymer J., 11, 64 (1979).)

Improved versions of the reactive acrylics have been developed and are called "aerobic" acrylics (61,62). These aerobic acrylics have diminished sensitivity to air inhibition and can be cured between two surfaces, regardless of the presence or absence of air. The adhesives are low in odor, nonflammable, and low in toxicity. The fast curing rate, e.g., 10 to 60 seconds, and the solvent-diluted activator minimize the movements in the substrates prior to fixture. The compositions, as claimed in patents (66,67), contain an elastomer that is colloidally dispersed in a monomer or in a monomer/oligomer/polymer solution. On the general subject of the rubber-reinforcement of acrylics, Drake et al. have written a recent review (68). However, they emphasize nitrile rubbers.

Several recently developed epoxides deserve mention. Dow has introduced a series of new experimental resins based on triglycidylether of tris(hydroxyphenyl)methane isomers and higher oligomers (73):
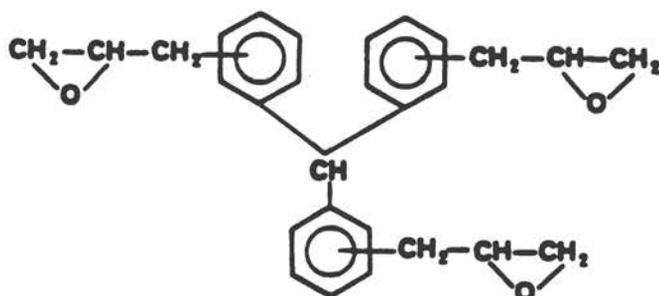
The cured epoxies have high heat distortion temperatures and improved thermal stability compared to types of epoxy resins. As for adhesives, Dow XD-7342.00L semisolid resin gives toughness, high wet strength, and long-term high-temperature oxidative resistance.

The literature describes a room-temperature curing epoxide made by converting a part of the epoxy function into episulfide by the addition of NMBTT (N-methyl-benzothiazole-2-thione) (74).
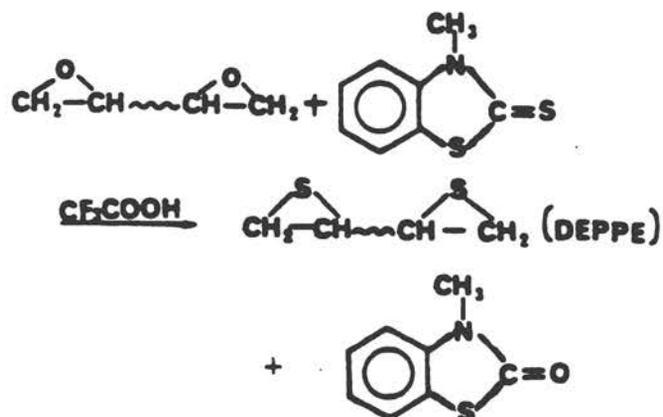
The resultant product (74) can be cured into a "bond cement" in 5-20 minutes at room temperature.

Another interesting low-temperature cure system (75) contains an epoxy resin - triglycidyl p-minophenol (TGPAP)
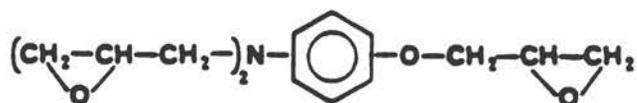
and BTDA as the curing agent.
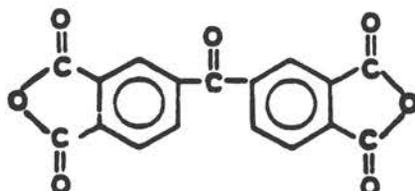
No other catalyst is needed. Solubilization of BTDA in the epoxide may be aided by slightly warming the mixture or by the addition of a mono anhydride, such as maleic anhydride (MA). The cured resin has high-temperature properties.

Among new epoxides are two families containing fluorine
and phosphorous, respectively. The fluoro-epoxides pre-
pared by Griffith (76,77) at the Naval Research Laboratory
have the following general structure:
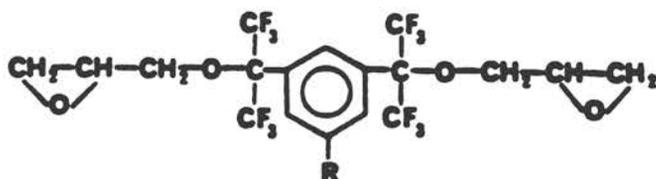
These epoxies are extremely low in water absorption and show
good resistance to biological fouling. Thus, they are
suitable for marine coating and underwater composites (78),
in addition to being water-resistant adhesives.

Besides fluoroepoxides, fluoroanhydrides (76,79) have
been synthesized. The structure of the substituted
p h t h a l i c anhydride is as follows:
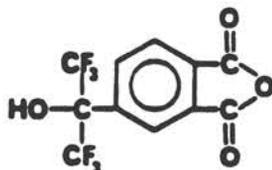
Other fluoroanhydrides can be derived from trimellitic and
pyromellitic anhydrides.

The phosphorous-containing epoxides (80) are good,
flame-resistant materials, especially when used for
structural adhesives. A typical phosphorylated epoxide is
based on bis-(3-glycidyloxyphenyl)methyl phosphine oxide
(BGDDPMPO):
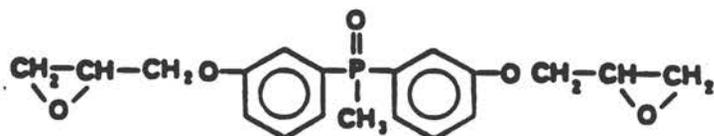
The phosphorylated epoxide is low in smoke evolution, high
in char yield, and high in oxygen index.

The structural adhesives discussed in this section are
acrylics, anaerobics, cyanoacrylates, and epoxies. Among
them, epoxies still are the most important. With new
innovations, epoxies will be more readily cured at room
temperature to compete with cyanoacrylates and anaerobics.
In the following sections, we shall discuss several new
forms of adhesives, e.g., hot-melt adhesives, film
adhesives and waterborne adhesives. Several structural
adhesives will be discussed again in relation to new forms
of adhesives.

VII.   HOT-MELT ADHESIVES

Hot-melt adhesives are currently one of the fastest
growing segments of the industry (Fig. 14). No solvent
discharge is the best answer to the pollution problem and,
in comparison with the waterborne systems, hot-melts
require less energy. From a capital investment standpoint,
the installation of a hot-melt coater line does not require
a large oven to remove water or solvent from the system. As a
result, hot-melt adhesives have been widely used, e.g., the
PSA's (81). Some of the hot-melts can be cured by uv
radiation or electron beams.
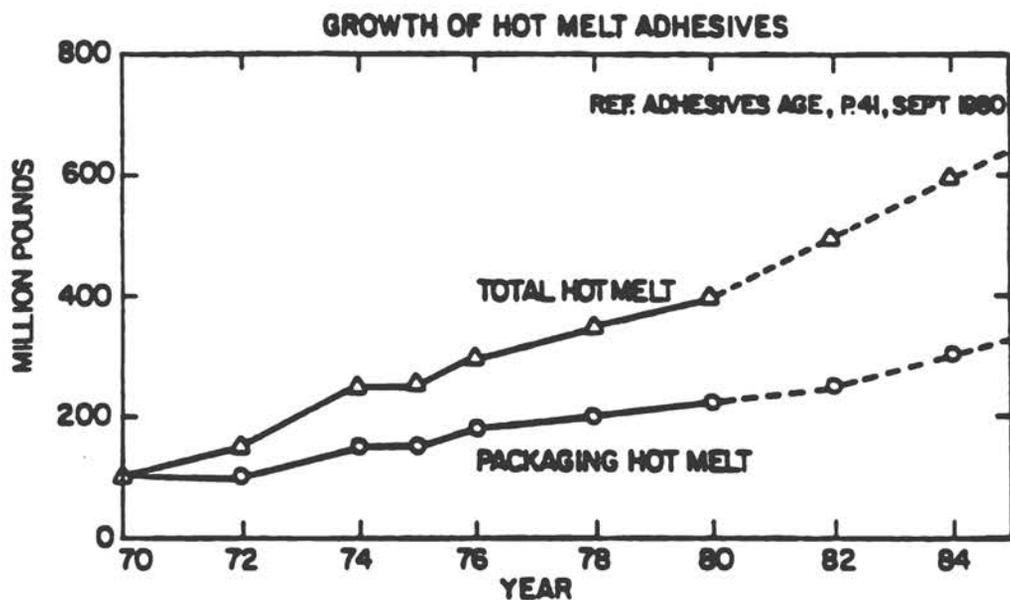
Fig. 14. Growth of Hot-Melt Adhesives (1970-1984)

The adhesives industry recognizes several advantages (81) in using PSA's:

. Increased production rate via elimination of the vehicle removal step

. Lower process energy demand

. Potential for heavy deposition and easy pattern coating

. Ready compliance with environmental protection regulations

However, the early systems had three major problems:

. Excessive thermoplasticity

. UV, heat, oxidation degradation susceptibility

. Limited plasticizer resistance

Significant improvements have eliminated the first two problems. Research is still being undertaken to solve the third problem.

Most hot-melts are based on polyolefins. The best known hot-melt is ethylene-vinyl acetate copolymer (EVA), e.g., duPont Elvax. In 1983, duPont added a new line of resins (82) designated as Elvax II ethylene copolymers. This family of copolymers contains a substituted alkyl group and an acid functionality. These resins are thermally stable and compatible with essentially all materials currently used in hot-melts. The acid functionality improves adhesion of the resin and enhances mechanical properties, e.g., toughness. Furthermore, the resins are cross-linkable through the acid groups.

Acrylic PSA's offer uv stability, color stability, clarity, and good adhesion. The recent development of hot-melt acrylics for PSA's deserves attention. However, the problems with using acrylic HMPSA's are many (83). For example, good cohesive strength is difficult to achieve in acrylic HMPSA's, especially at elevated temperatures, in a product that can be applied satisfactorily in melt form.

Some problems of acrylic HMPSA's are circumvented by formulation. For example, the addition of vinyl

toluene/alpha-methyl styrene tackifier resin, Piccotex LC (Hercules), can enhance peel adhesion, and reduce melt viscosity with no loss in uv resistance. New lines of acrylic HMPSA's have been reported (83), but further development is needed to warrant acrylic HMPSA as a competitive adhesive.

One of the new developments in hot-melts is the application of foam technology. Several years ago, the Nordson Laboratory (84,85) discovered that the foamed hot-melts are easier to spread than the non-foamed hot-melts. Later, foamability (86) studies were carried out for the following hot-melt adhesives: polyethylene, polypropylene, polyamide, ethylene-vinyl acetate copolymer, and polyester. Air, CO_2, and nitrogen were used as the blowing gases; various types of surfactants were used for dispersion.

A two-step gear pump (Fig. 15) was used to introduce the gas into the hot-melt adhesive. Foamability was later found to vary with the polymers used. Polyethylene is excellent for foaming. Polypropylene, polyester, and 12-polyamide (Nylon 12) are also very good. Styrene-butadiene and ethylene-vinyl acetate are good and dimer acid polyamide is fair.

Hot-melt foams should have many useful applications in: appliances, automobiles, bag manufacture, book manufacture, cans and closures, case forming and sealing, manifold business forms, disposables, roll wrapping, and metal building fabrication. The greatest potential use for hot-melt foams is in new applications where hot-melt adhesives have not been used before.

A new technological development for hot melts is their application by robotics (87). Robotics have been used to apply hot melts to structural components, e.g., fiberglas-reinforced components. In one case, structural adhesives are applied at 480°F (249°C) with a specially designed hot-melt dispenser and gun marketed by Monsanto Co. Robotics have also been used to apply hot melts to make PSA's. Robotics are useful in applying hot-melts to gaskets and seals. In general, robotics provide higher productivity, improved quality, and reduced cost.
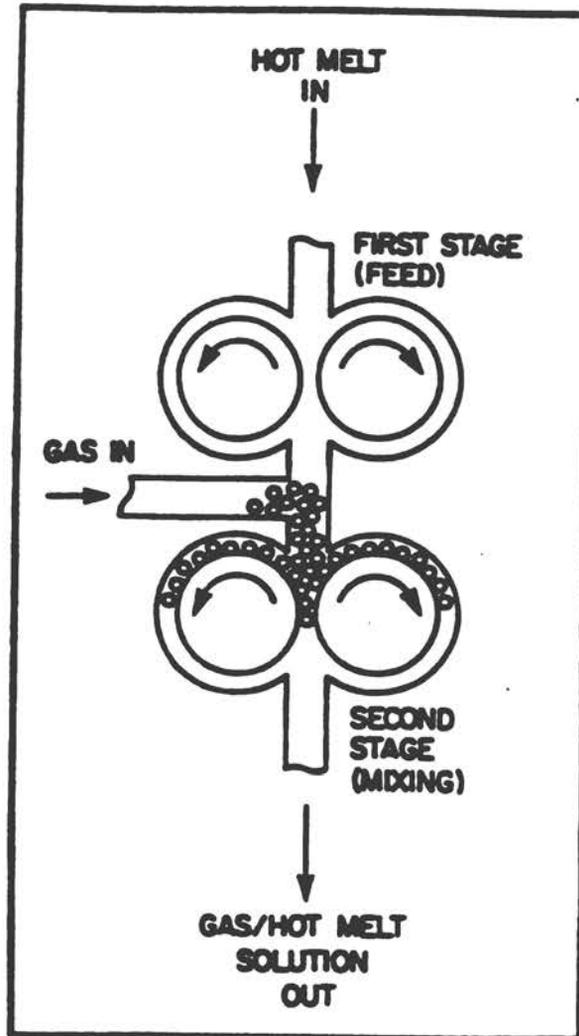
Fig. 15. Hot-Melt Foaming Process

(Ref: F. T. Hughes, Adhesives Age, <u>25</u>, No. 9, 25 (1982).)

VIII. FILM ADHESIVES

In addition to hot-melt adhesives, film or sheet adhesives (88,89) have been used for the same purpose in eliminating solvent pollution. The adhesive-bearing films, such as PSA, can be cut to size and applied between mating surfaces. Curing, if necessary, can be carried out in the usual manner. Thus today, coated film adhesives can be used for large structural parts to replace solvent-borne adhesives.

Hot-melts, radiation-curable adhesives, and epoxies can all be applied to a substrate in film or sheet form. The substrate can be metal, plastic, or paper. In addition, the substrate can be woven, nonwoven, or knot. The porous substrates can be used to manufacture filter aids or medical adhesives, e.g., to attach prostheses to the skin. An interesting form of substrate is a foam that joins surfaces of irregular gaps. The foam can also be formed instantaneously during curing to fill gaps.

A recent development is the use of more than one adhesive on the same substrate. For example, a cross-linkable acrylic adhesive can be applied on a close-cell polyurethane foam, and the sheet adhesive can be used to mount autobody side-moldings. A two-sided film or sheet can be made to contain a thermoplastic adhesive on one side to bond to the auto-carpet fibers and another adhesive on the opposite side to bond to the polypropylene body and console panels.

The use of film adhesive in the aerospace industry will be discussed in a forthcoming section.

IX. WATERBORNE ADHESIVES

As discussed in the Introduction, in addition to hot-melt adhesives, one of the most important forms of adhesives for the future is the waterborne system. In general, an advantage of the waterborne system is that it is free from the solvent-pollution problem. For this reason, we shall describe several new waterborne systems in detail: acrylics, modified ethylene-vinyl acetate, polyurethanes, phenolics, epoxies, isocyanates, and tackifiers. Applications of these systems range from PSA's contact adhesives, and laminating adhesives to wood adhesives.

Acrylics

For PSA's, acrylic latexes(83) appear to be the most promising compounds because of their uv and thermal stability, and high resistance to the plasticizer migration from vinyl substrates. Acrylics also offer advantages in lower formulating and manufacturing costs.

A new acrylic family (83) was developed specifically for low surface energy surfaces, e.g., polypropylene. A new

form of cure, a "low energy cure" or LEC polymer, can take place at low temperatures. The LEC catalysts are generally alkaline, e.g., sodium sesquicarbonate. The LEC polymers provide rapid water release and unique adhesion to glass surface. These polymers can also be used for lamination.

For contact adhesives, acrylic latexes compare favorably to Neoprene A latex as well as to the solvent-based Neoprene. As expected, the latexes dry slower than the solvent-based Neoprene; however, the drying time can be shortened through formulation. In terms of lap shear adhesion, acrylic latexes are better than Neoprene A latex. In addition, acrylic latexes offer comparable performance, freeze-thaw stability, nonflammability, ease of handling, and ease of cleanup.

For lamination, waterborne adhesives have actually been used in manufacturing flexible packaging and industrial laminates (91). Other latexes used besides acrylic are vinyl acetate, ethylene-vinyl acetate, vinylidene chloride, etc. The flexible packaging systems using these adhesives are: PVDC-Cello/LDPE, OPP/OPP, polyester/LDPE, and metallized polyester/LDPE. Similarly, industrial laminates using these adhesives are PE/textile/PE, OPP/printer paper, and polyester/printed Tyvek (PE).

Polyvinyl acetate

A conventional emulsion polymer based on vinyl acetate has been modified by carboxylation (92). The carboxylated ethylene-vinyl acetate adhesive increases the adhesion to metal and polymer surfaces and the resistance to oil, grease, and water. The films are also acid, alkali, and uv resistant. Furthermore, the polymers are cross-linkable through the carboxylic groups. These adhesives can react with aminoplasts, phenolics, and epoxy resins for increased water and creep resistance.

Polyurethanes

One of the most interesting waterborne systems is polyurethane (93). Polyurethane dispersions can be made by the following processes (94): acetone, prepolymer mixing, melt-dispersion (95), self-dispersion of solids, ketimine process (96), and ketazine process (97). The acetone

process involves the formation of an ionomer first in organic solvent and then in a dispersion in the acetone-H_2O mixture (8:2). In the prepolymer-mixing process, a prepolymer containing an ionic group terminated with isocyanate groups can form a spontaneous dispersion upon the addition of water. The polyurethane urea-ionomer dispersion is illustrated in Fig. 16.

In the melt-dispersion process (95), an NCO-terminated prepolymer is prepared next from a polyester or polyether diol, a diisocyanate, and a glycol containing a potential ionic group. The NCO/OH is between 1.2 and 1.8. Then, the prepolymer is terminated with urea to form biurets, which are further alkylated to give an ionomer as shown in Fig. 17. The bis-biuret can be considered to be somewhat hydrophilic to be methylolated with formaldehyde. Upon dilution with water, a stable dispersion is formed.
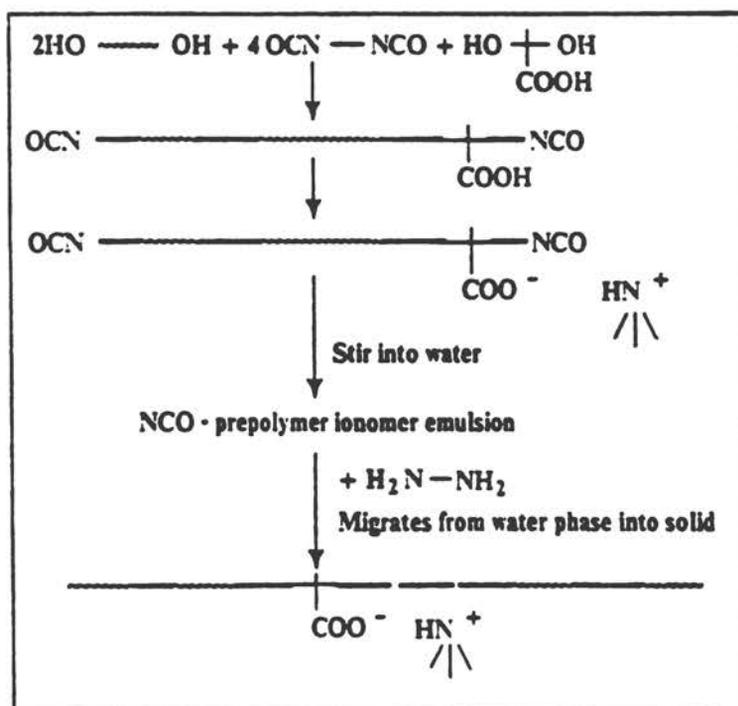
Polyurethane-Urea Ionomer Dispersion

Fig. 16. Prepolymer-mixing Process for Polyurethane Urea-ionomer Dispersion

(Ref: D. Dietrich, Prog. Org. Coatings, 9, 281 (1981).)

OCN —— NCO + HO —— OH + OCN —— NCO + HO —N—OH + OCN —NCO

(NCO/OH = 1.5)

OCN ————————— N —— NCO

+ H₂N –CO –NH₂
+ Cl–CH₂ – CO –NH

$$H_2N-CO-NH-CO-NH \text{————————} \overset{(+)}{\underset{CH_2-CO-NH_2}{N}} \text{————} NH-CO-NH-CO-NH_2 \quad Cl^-$$
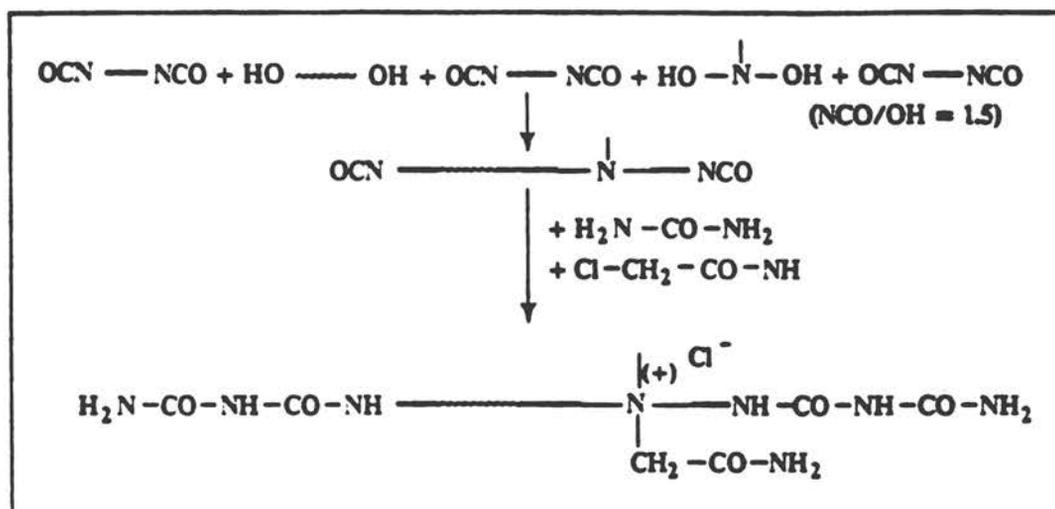
Fig. 17. Formation of Self-Dispersible Oligomer

(Ref: D. Dietrich, Prog. Org. Coatings, 9, 281 (1981).)

The ketimine process combines the quality and versatility of the acetone process with the simplicity and economics of the prepolymer mixing process. Ketimines are formed from a ketone and diamines (96).

$$H_2N-R-NH_2 + 2OC\overset{R_1}{\underset{R_2}{<}} \rightleftharpoons \overset{R_1}{\underset{R_2}{>}}C=N-R-N=C\overset{R_1}{\underset{R_2}{<}}$$

+ 2H₂O
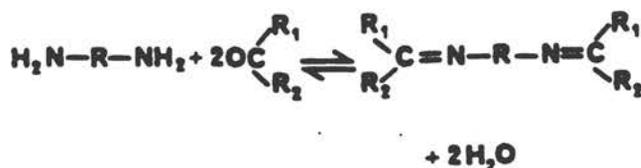
The ketimines can then be mixed with NCO prepolymers without inducing a reaction. However, upon the addition of water, a dispersion results and, about the same time, the ketimine is hydrolyzed to free the amine. The amine then undergoes chain extension to produce a material that can also be obtained by the acetone process.

In the ketazine process (97), the NCO prepolymer is mixed with a ketazine, aldazine, or hydrazone before dispersing. Upon the addition of water, hydrazine is liberated to promote chain extension:

$$R_1 \backslash C = N - N = C / R_1$$
$$R_2 / \qquad \backslash R_2$$

$$R_1 - CH = N - N = CH - R_1 \xrightarrow{\ H_2O\ } H_2N - NH_2$$

$$R_1 \backslash C = N - NH_2$$
$$R_2 /$$
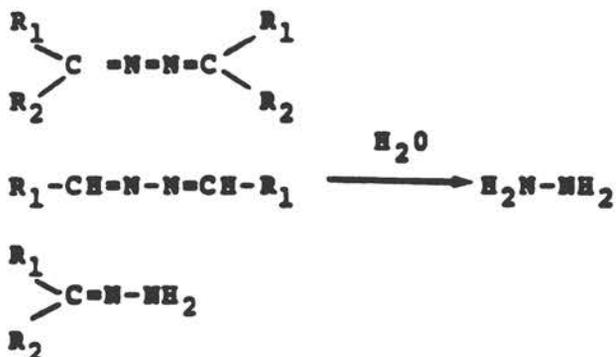
Phenolics

In the waterborne phenolic adhesives, a new dispersion system (98) has been reported. This system uses the solubility of some thermoplastics in phenol, and the subsequent polymerization takes place upon the addition of formaldehyde, an emulsifier, and water. The dispersion is then formed in situ. The versatility of this process is indicated by the use of many polymers with a wide range of properties, e.g., polyvinyl formal, polyvinyl butyral, acrylonitrile-butadiene copolymer, bisphenol-A resins, polyvinyl acetate, polycarbonate, polymethyl methacrylate, and nylons.

The resultant polyblends are generally two-phased and contain discrete particles dispersed in the phenolic matrix. With the reinforcements, the waterborne phenolic can compete with the solvent-borne counterparts. Thus, some of them can be used as metal-bonding adhesives.

Epoxy Resins

Waterborne epoxy resin (99) has been used for lamination. The epoxy copolymers PD-6049 and PD-4070 are supplied by Celanese at 69% solids in glycol ether co-solvents, which can readily be dispersed with water. When the dispersion is formulated with an aminoplast catalyst, curing takes place in several seconds at 450°F (232°C). The dispersion has excellent adhesion to paper, PET film, and aluminum foil.

Isocyanates

As wood adhesives, isocyanates have found applications as binders for composition board (100). The advantages of isocyanates are many: high adhesive and cohesive strengths, flexibility in formulation, versatility of various cure temperatures and curing rates, excellent structural properties, ability to bond with material having moisture content, and lack of formaldehyde emission. The most important advantage is their ability to form waterborne adhesives.

Emulsion-polymer isocyanates (EPI's) were introduced by Ashland Chemical Co. as better performing wood adhesives (101). EPI's are equivalent to phenol-resorcinol and cross-linkable polyvinyl acetate adhesives. EPI's are more advantageous than others because they have shorter press times, no chalking temperature, a low-temperature curing, no formaldehyde emission, better resistance to high temperatures and accelerated aging, environmental attractiveness, an ability to determine performance by adjusting hardener level, and more tolerance to variations in process conditions.

Waterborne Tackifiers

For PSA's with the resin-rubber systems, several types of latexes are being used in place of rubber for the waterborne adhesives. Styrene-butadiene (102) latexes and natural rubber latexes (103) have been mentioned in the literature. In addition, waterborne tackifiers (104) have been developed for PSA's. A family of emulsifier-free, high solids, completely freeze-thaw stable tackifying resins was developed by Rohm and Haas. The new products are viscous resins based on the replenishable tall-oil rosin. The

resins can spontaneously disperse in water without the addition of a surfactant or a solvent. Other waterborne tackifying resins developed by Hercules have been discussed by Jones (105).

Phenolic tackifiers (106) in the form of dispersions can be used to formulate neoprene or acrylic latex into waterborne contact adhesives. For example, a solid ratio of latex and phenolic dispersion (Union Carbide-BKUA-2370 or BKUA-2260) of 3:1 can form a stable adhesive at pH 6.0-6.5.

The increasing amount of research in waterborne systems should some day overcome technological difficulties. However, the change-over from some solvent-borne to waterborne systems has presented difficulties (107), for example, poor coating quality, excessive foam, insufficient water resistance, and even some corrosion and clean-up problems. Despite the problems, some waterborne systems have already been adopted for the manufacture of PSA's, contact adhesives, laminating adhesives, and wood adhesives. However, few applications of the waterborne systems as structural adhesives, especially as aerospace structural adhesives have been found.

X. AEROSPACE STRUCTURAL ADHESIVES

A special study on aerospace structural adhesives was conducted in 1976 by the National Materials Advisory Board of the National Research Council. The final report was published as one of the series in Treatise on Adhesion and Adhesives (108). That report discussed primarily phenolic and epoxy-based materials, e.g., vinyl-phenolics, nitrile-phenolics, epoxy-phenolics, nylon-epoxies, and elastomer-epoxies. Polyimide and polybenzamidazole adhesives were barely mentioned. Most of the high-temperature adhesives discussed in one of the preceding sections were either not invented or not developed at that time.

Today with the advance of structural and high temperature adhesives, aircraft, spacecraft, and missles (109) are built with secondary-bonded and some primary-bonded structures. The PABST (Primary Adhesive Bonding Structures Technology) program (110) was carried out at the Air Force Materials Laboratory between 1976 and 1981. That project led to the construction of a totally adhesive-bonded 42-foot-long circumferential fuselage section of a

McDonnel Douglas YC-15 military aircraft. Epoxy adhesives
replaced panel bolts and rivets; the bonded panels were
cured in an autoclave. After 120,000 hours of testing, the
flaws did not grow into catastrophic proportions as in the
case of riveted structures.

Bonded fuselages were not the only primary structures
studies; bonded fuel-carrying wings were investigated in
the same laboratory. One was the epoxy-bonded aluminum
laminate for the lower skin of a seven-foot wing section of
F-16 fighter and another was the AWT (Advanced Wing
Technology) for the 10-foot-long section of a bomber wing
that used epoxy-bonded aluminum laminate in the lower skin.
The latter was tested with simulated fuel inside the "wet"
wing. The test showed that rivetless wing bottoms enhanced
the fuel containment of the wings and minimized fuel leak,
just as riveted structures did. The adhesive bond did not
fail even after other failures occurred at the end of the
aircraft two-lifetime testing. Furthermore, the adhesive-
bonded structures were at least 10% lighter than the riveted
structures.

At the end of the PABST program, there were several
questions unanswered about: (1) the ease and cost of
maintaining the adhesive-bonded structures, (2) the
durability in actual service environments where
temperature cycles and moisture attack could reduce the life
of the bonded joints, and (3) the feasibility and cost of
curing an immense primary-bonded structure in an autoclave.

To solve the third problem, other approaches have been
considered. One of them is the application of weld-bonding
(111). The metal parts, with a paste adhesive sandwiched in
between, are spot-welded by two electrodes that exert
pressure on both sides. Then a current is passed through the
electrode to cause the neat resin to melt and weld the parts
at the electrode contact point. The curing process can then
be continued in a regular oven. This process has actually
been used by the Air Force to build an epoxy-bonded 100-
square-foot forward fuselage section for the C-130H
transport aircraft. After eight-years monitoring over
6,000 flight hours, the structure performed very well.

For film adhesives, ultrasonic welding (112) at a
frequency of approximately 15,000 kHz can be used instead of
weld-bonding. The subsequent curing can also be completed

in a regular oven. This technique has been applied to small access panels for the Air Force A-10 attack aircraft at Fairchild Republic Co. Plans are underway to treat large fuselages and fuselage doors by the same weld-bonding method.

In the future, some of these new techniques will be used to cure high-temperature adhesives for building aircraft without rivets or bolts. In addition, with the advance of many low-temperature curing methods, the processing may be made simpler for metal-to-metal, metal-to-composite, or composite-to-composite structures.

One of the major problems with structural adhesives is durability. Many publications have been written on this subject. Recently, Kinloch (113) published a very timely book about this topic. A symposium proceedings volume on Adhesive Joints (114) is due to appear sometime this year. Thus, it is not our intention to devote any length of this review to this topic; however, there are several papers that need to be mentioned related to high-temperature adhesives. Hendricks and Hill (115) reported the evaluation of high temperature structural adhesives for extended service. Helminiak and Jones (116) studied the influence of the molecular weight of polyphenylquinoxaline thermoset on fracture behavior. Burks and St. Clair (117) mentioned the effect of molecular weight on the melt viscosity and fracture energy of BDSDA/APB, polyphenylene ether sulfideimide. Some of these polymers could be the aerospace structural adhesives of the future.

In addition to adhesives, the aerospace industry also needs conventional sealants and special sealants to withstand the temperature extremes of the aerospace environments. Both these subjects will be discussed in the following sections.

XI. CONVENTIONAL SEALANTS

High quality, conventional sealants (118) will dominate the industries in the 80's. Energy-efficient, water-proof, and durable sealants will be in demand by the construction and automotive industries. Commonly used sealants are polysulfides, polyurethanes, silicones, oil-based caulks, butyls, and solvent or latex acrylics. However, judged by their performances and durability (Table 3), the first three will be the most important sealants for this decade.

Table 3. Comparison of High Performance Sealants

	2-Part Polysulfide	1-Part Polysulfide	2-Part Urethane	1-Part Urethane	2-Part Modified Urethane	1-Part Silicone
Cure rate	M – hr	S – several hr or days	M – hr	S – hr	S – days	Fa – min or hr
Service temp range, $^{\circ}F$	$-20,-40^{\circ}$ $+180^{\circ}$	$-20,-40^{\circ}$ $+180^{\circ}$	$-20,-50^{\circ}$ $+180^{\circ}$	$-20,-50^{\circ}$ $+180^{\circ}$	-65° $+180^{\circ}$	-65° $250-425^{\circ}$
Movement capability based on joint dimensions	$\frac{+12.5}{+25}$	$\frac{+12.5}{+25}$	$\frac{+25}{+30}$	$\frac{+25}{+35}$	$\frac{+25}{+35}$	$\frac{+25+40}{+50+100/-50}$
Abrasion	G	G	E (very tough)	E (very tough)	E (very tough)	F
Weatherability for sealing & caulking	G	G	E	E	E	E
Other unique features	Some are acceptable for underwater use on concrete.		Now being tested for underwater use on concrete – each will probably require special primer.			
	Compatible to all or most substrates.		Compatible to all or most substrates.		Most are compatible to all or most substrates. Some, the acid cure, cannot be used on concrete, marble, and certain metals.	

Note: E = Excellent; G = Good; F = Fair; M = Moderate; S = Slow; Fa = Fast
(Ref: J.M. Klosowskii, Adhesives Age 24, No. 11, 32 (1981).)

For durability, the polysulfides are designed to last for 10 to 20 years in outdoor environments. The poly-urethanes should last 20 years, and silicones should have a life longer than 20 years. One of the problems with polysulfides is that they have the largest compression set of the three, causing joint failure, especially in winter months. With the trend toward narrower and prettier joints, the polysulfides (65 to 75 percent recovery) are being out-performed by the polyurethanes (85-95 percent recovery) and the silicones (90-100 percent recovery).

Besides durability, premium sealants are judged by special properties as shown in Table 4. The ability to take on greater elongation and compression is measured by movement capability in terms of joint width. The stability to uv exposure is important for those glazing and insulation compounds used in modern high-rise structures. Thermal stability is in demand for solar collectors, or for other structural materials. On the basis of these evaluations, we can foresee future trends of sealants as shown in Table 4. Silicones appear to out-perform others. In the meantime, technical advances will provide low-modulus polysulfides, and better movement ability for both polysulfides and polyurethanes. Their cure time will be decreased and the uv stability will be improved to match or compete with silicones. All three will be developed for better adhesion under the un-primed conditions.

For highway sealants (119), the desired properties are: adhesion (without primer), weatherability (adequate retention of properties for more than 10 years), resilience, temperature stability, hardness range for hot or cold (firm enough to resist incompressibles, puncture and tear resistant), good uncured consistency, solvent resistance, repairability, and abrasion resistance. Silicones, especially those of low-modulus, offer nearly all the properties desired as a good highway sealant.

Now many composite materials are used in aircraft (Fig. 18). Graphite/epoxy and graphite/Kevlar are commonly used. For these materials, polysulfides (120) have been used as sealants. To provide airframe integrity, everything has to be sealed, preferably with flexible sealants that allow joint movement, fuel and weather resistance, and corrosion prevention. Today airframes are guaranteed to have a service life of 20 years without any corrosion damage. For this reason, the inhibited polysulfides are used to prevent corrosion between aluminum and graphite/epoxy composite parts.

Table 4. 10-Year Forecast for Sealants

	Gain	Loss	Maintain	Overall
Silicones	Expansion joints and perimeter sealing market. Insulated glass market - secondary seal. Structural glazing – no competition. Solar glazing and sealing markets. Do it yourself market. Highway sealant market. Industrial adhesive/sealing markets.	-	Form-in-place gasket market share. Aerospace and specialty sealing market share.	Some fast and some steady gains in volume and market share.
Polyurethanes	Expansion joint and general sealing markets. Structural adhesive seal - non-glazing	-	Pedestrian traffic sealing market	Gain volume and market share, mostly from polysulfides.
Polysulfides	Volume gains in insulated glass.	Market share for insulated glass. Glazing market. General sealing and expansion joint market.	Specialty market - industrial, fuel tank, for example.	Slow decline in most areas
Butyls	Insulated glass primary and secondary seal. Do it yourself market from oil-based caulks.	Mobile home sealing. Do-it-yourself market to silicones and urethanes.	-	-
Acrylics Solvent	-	Will show decline in all areas.	-	-
Latex	Do it yourself market gain from oil based loss to silicones	-	-	Steady market – no growth.

*All gains and losses refer to gains in both volume and market shares except where specifically noted

(Ref: Adhesives Age, November 1981)
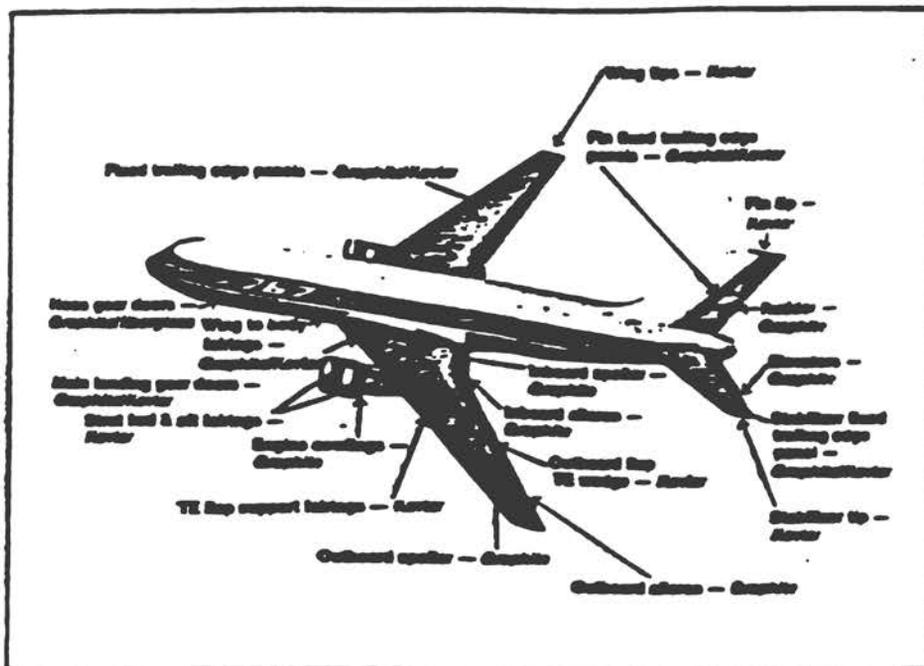
Fig. 18. Composite Applications for the Boeing 767.

(Ref: G. Graff, High Technology, 67, Sept. 1983)

Most conventional, polysulfide sealants are based on disulfides. Recently, a new family of sulfur-containing sealants (121,122) has been developed based on thioethers (Fig. 19). The thioether structure is thermally more stable than the polysulfide, thus the upper operating temperature of the former is $60^{\circ}-70^{\circ}F$ $(26.6^{\circ}-31^{\circ}C)$ higher than the latter. Moreover, the thioethers show better hydrolytic stability and chemical resistance than the disulfides. A product based on thioether, Permapol-3, is now available from Products Research & Chemical Corp. Permapol-3 can also react with urethanes or epoxies to form blended adhesives and sealants.

Though thioether sealants are somewhat more thermally stable than polysulfides, they are still not qualified as the advanced sealants for aerospace applications in severe environments. In the following section, we shall discuss some of the advanced sealants being considered for future applications.
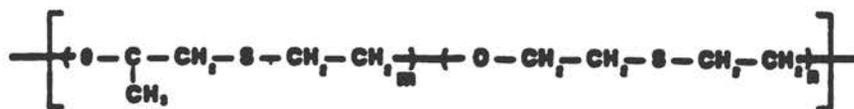
PERMAPOL P-3 POLYMER

POLYSULFIDE POLYMER

Fig. 19. Structures of Polythioether and Polysulfides

(Ref: J.W. Huff and H. Singh, technical publication by Products Research & Chemical Corp.)

XII.   ADVANCED SEALANTS FOR AEROSPACE APPLICATIONS

For aerospace applications, several advanced sealants have been mentioned: cyanosilicones (123),fluoroalkyl-arylenesiloxanylene (FASIL) (124), phosphonitrilic fluo-roelastomers (PNF®) (125,126), flexible polyimide (127), tetrafluoroethylene oxide phenylquinoxaline elastomer (PEX) (128), perfluoroalkyl ethers (129), etc. These advanced sealants have been used for fuel tank sealing, channel sealing, filleting, aerodynamic smoothing, and other assemblies. Basically, they should be high-temperature, serviceable, fault-tolerant, and adhere well to metals and/or composites.

Cyanosiloxane Sealants

For space shuttles, a special type of sealant, cyanosiloxane (123) was found to be unique and operational. Cyanosiloxanes can be synthesized by the catalytic addition

of an unsaturated nitrile to a methyl hydrogen polysiloxane
(Fig. 20). At the end of the reaction, at least one
unreacted -Si-H (hydride) bond remains per molecule. This
bond is subsequently hydrolyzed to -SiOH, which then
undergoes a condensation to give a high molecular weight,
but not cross-linked, polymer (Fig. 21). The polymer is a
clear, dark brown, thick liquid with a viscosity of 5,000
poise. At room temperature, a liquid-gel transformation
can take place but the gel can reversibly transform into the
liquid under shear. The polymer is resistant to hot
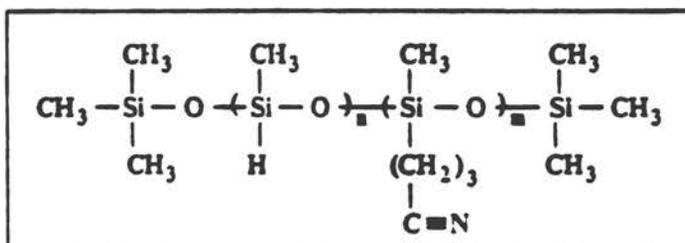hydrocarbon fuels, but soluble in polar solvents.

Fig. 20. Structure of Polycyanosiloxane
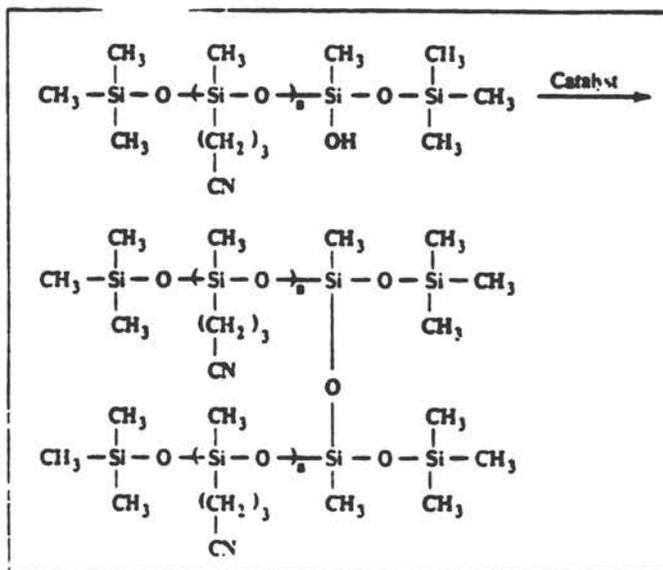(Ref: H. Singh, Adhesives Age, 21, No. 4, 24 (1978).)

Fig. 21. Reaction to Increase Molecular Weight of the
Polycyanosiloxane Polymer
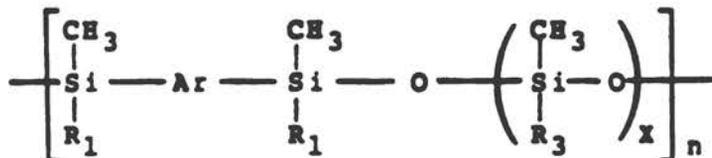(Ref: H. Singh, Adhesives Age, 21, No. 4, 24 (1978).)

The glass temperature of this polymer is $-60^\circ F$ $(-51^\circ C)$. When exposed to $350^\circ F$ $(177^\circ C)$ for 48 hours, no curing takes place. The sealants from this polymer are also not cured even in the presence of oxygen at $450^\circ C$ $(232^\circ C)$. They appear to be somewhat rubbery and remain flexible to $-60^\circ F$ $(-51^\circ C)$.

Two products, PR-711 and PR-719, are manufactured by Products Research Chemical Corp. PR-711 was used for environmental sealing of structural faying surfaces of the first two flights of the space shuttle orbital airframe. PR-719 is designed to seal integral fuel tanks of aircraft. The sealant has to be a non-curing type so that the channel can be resealed without disassembling the structure.

Fluoroalkylarylenesiloxanylene (FASIL) Sealant

FASIL was developed at the Air Force Materials Laboratory. This elastomer has a broad temperature servicing range: $-54^\circ C \longrightarrow 260^\circ C$ $(-66^\circ \longrightarrow 500^\circ F)$. It has excellent adhesion to Ti and Al; it is JP-4 fuel resistant and hydrolytically stable.

Two classes of FASIL elastomers have been chosen for preliminary evaluation: the methyl- and 3,3,3-trifluoro-propyl-substituted poly(m-xylylene siloxanylenes) (129) and the corresponding poly(m-phenylene siloxanes) (124). The general formula of FASIL is as follows:

$$\left[\begin{array}{c} CH_3 \\ | \\ Si \\ | \\ R_1 \end{array} - Ar - \begin{array}{c} CH_3 \\ | \\ Si \\ | \\ R_1 \end{array} - O - \left(\begin{array}{c} CH_3 \\ | \\ Si \\ | \\ R_3 \end{array} - O\right)_X \right]_n$$

where R_1, R_2, and R_3 are either methyl or 3,3,3-trifluoropropyl and X=0, 1 or 2; Ar is either m-phenylene or m-xylyene.

Phosphonitrilic Fluoroelastomer (PNF ®)

Another fluorine-containing polymer, phosphonitrilic fluoroelastomer (PNF ®) (125,126) is prepared from a soluble precursor, chlorophosphazene and a mixture of fluorinated alkoxides containing 65% trifluoroethoxide and 35% telomer fluoroalkoxides. The structure of PNF is:

$$\left(N\!=\!P\right)_{n} \begin{array}{c} O\ CH_2CF_3 \\ | \\ | \\ O\ CH_2(CF_2)_X\!-\!CF_2H \end{array}$$
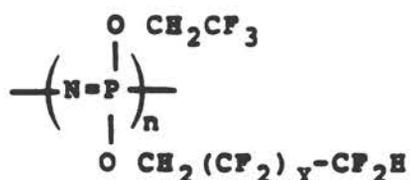
where X can be 1, or 3, or 5......

This polymer contains approximately 55% fluorine and a small number of unsaturated sites for cross-linking. The fluorine content imparts outstanding resistance to fuels, including JP-4 fuel, oils, most hydraulic fluids and chemicals. The glass temperature is $-68^{\circ}C$ $(-91^{\circ}F)$ and thus it allows the service temperatures to be as low as $-65^{\circ}C$ $(-85^{\circ}F)$. The upper service temperature is $175^{\circ}C$ $(347^{\circ}F)$.

Since the structure contains very few weak links, it is oxidative and ozone resistant. The unique mechanical properties are low compression set, high modulus, excellent flex fatigue, and good abrasion resistance. Thus, it has been evaluated as an advanced sealant for aerospace applications.

Flexible Polyimide Fuel Tank Sealants

The requirements for the fuel tank sealant (127) were:

- Compliant elongation to break (>50 percent)
- High-temperature stability $\left[450^{\circ}F\ (232^{\circ}C)\ to\ 600^{\circ}F\ (316^{\circ}C)\right]$
- Low-temperature flexibility $\left[-50^{\circ}F\ (46^{\circ}C)\ to\ -60^{\circ}F\ (-51^{\circ}C)\right]$
- Titanium compatibility and adhesion
- Aliphatic/aromatic (JP) fuel stability
- Low-cure temperature $<400^{\circ}F$ $(204^{\circ}C)$
- Useable at high resin solid content in non-toxic solvents (>80% w/w)

To meet the above requirements, a synthetic approach based on the Diels-Alder addition was used. The key monomers were chosen from the three monomers shown in Fig. 22.

Name of monomer	Abbreviation of monomer	Structure
Bis(furfuryl) imide of Bis[4-(3,4-dicarboxy-phenoxy)phenyl]sulfone Dianhydride	BFBSI	
Bis(4-maleimidophenyl) Methane	BMPM	
Bis(maleimide) of Jeffamine ED*	BMJEF	

*Repeat units a, b, an c are integers yielding molecular weights of approximately 900, 900, and 2000

Fig. 22. Monomer for Flexible Polyimides
(Ref: R.J. Jones and H.N. Cassey, Adhesives Age, 22, No. 11, 33 (1979).)

The reaction product between BFBSI and BMJEF gave a flexible polyimide sealant with the following properties:

. High-temperature fuel stability (500°F (260°C)
. Low-temperature flexibility (-50°F (46°C)
. Excellent JP fuel resistance
. High adhesion to AL and Ti substrates
. No stress-corrosion imparted to Ti surface
. Facile cure and processibility
. Available in 100 percent solid formulary
. Excellent tensile properties

Adhesives and sealants used for the aerospace structures must endure severe environments. Another family of adhesive materials has also been developed for solar collectors, presumably based on the same ability to endure severe environments. Though there are different kinds of severe environments, conventional polymers generally do not survive in the solar collector environment. We shall discuss those adhesive materials used for solar applications in the following section.

XIII. SOLAR COLLECTOR ADHESIVES AND SEALANTS

Adhesives for Solar Collectors

Adhesives (128) play an important role in the construction of a solar parabolic trough reflector. The adhesives should be compatible with silvered glass mirrors and should be able to carry structural loads. Moreover, the adhesives should be durable for at least twenty years without losing their properties. Adhesives screened for solar collectors were epoxies, urethanes, and acrylics. Three types of stress conditions were identified as the most likely causes of failure in the trough modules:

1. Thermal cycling

2. High temperature, low humidity: $160^{\circ}F$ ($71^{\circ}C$), low R.H. (e.g., R.H.-8%)

3. High temperature, high humidity: $160^{\circ}F$ ($71^{\circ}C$), high R.H. (e.g., R.H.-80%)

When a flat solar collector is used, a polymer film based on fluoropolymers, e.g., Tedlar ® polyvinylidene fluoride, has been used to make a laminate with an adhesive. The solar collector, so formed, is light-weight and low-cost.

Sealants for Solar Collectors

The sealant materials used for the solar collectors must be durable under harsh environments (132). They must be stable to air at high temperatures, which can exceed $200^{\circ}C$ ($392^{\circ}F$) for a short period or several weeks inside the cell. The temperature can vary between $125^{\circ}C$ ($257^{\circ}F$) and $200^{\circ}C$ ($392^{\circ}F$). In addition, high humidity, ozone, and ultraviolet radiation could shorten the service life.

Fluoroelastomers, silicone rubbers, butyl rubbers, ethylene-propylene terpolymer (Nordel), ethylene-acrylic copolymer (Vamac), and polyacrylate (Hycar 4054) were evaluated for the PS (preformed seal or gasket) compounds. After 32 days at $225^{\circ}C$ ($437^{\circ}F$), only the fluoroelastomer, Viton, appeared not to suffer any loss of tensile properties.

®Tedlar is a registered trademark of duPont Company.

For the intermediate caulking compounds (SC), acrylics still displayed a significant elongation after 32 days at $125^{\circ}C$ ($257^{\circ}F$). However, the accelerated hydrolytic stability of the acrylic is poor in comparison with that of the silicone (e.g., RTV 103).

The outgassing of sealants in the collector system is a serious problem (128). For this reason, the polymer was tested at $150^{\circ}C$ for several days. The condensate was collected and identified. The results indicated that only fluorocarbon did not outgas under the test conditions. In the case of silicones, during the outgassing, cyclic siloxanes were released through thermal degradation.

There may be some disadvantages to the fluorocarbons. The first is relatively high cost and the second is a then high compressive set at temperatures of $10^{\circ}C$ and lower, which could present problems in colder climates (134). Another study (135) of the edge seal indicated that butyl rubbers, if stabilized against uv radiation, were better than silicones and might be substituted for the high-cost fluoropolymers for that particular application.

XIV. CONCLUSIONS

In this brief review, we have attempted to demonstrate the importance of chemistry to the developments of new (or new forms of) adhesive materials. Much success has been achieved in the syntheses of polymers for aerospace adhesives and sealants. New or modified structural adhesives have been developed with improved mechanical properties and durability. However, there is still room for innovation for developing new adhesive materials for use under severe environments.

To counter energy-saving problems, low-temperature curing by radiation has gained acceptance. For a long-term solution of pollution problems, hot-melt adhesives and the waterborne systems are being increasingly used as a substitute for the solvent-borne adhesives. In the future, the waterborne systems could dominate the entire adhesive industry.

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