

PLASTICS, ADHESIVES AND COMPOSITE MATERIALS

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## PLASTICS, ADHESIVES, AND COMPOSITE MATERIALS

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### Introduction

The first large scale application of reinforced plastic materials in aircraft occurred almost twenty years ago when polyester resin laminates were used in radomes. The materials selection at that time was primarily based upon the required electrical transparency of such a material. For this particular application, the electrical properties continued to be highly important, but in addition the continued success in efforts to improve the structural efficiency of reinforced plastics has resulted in recognition and present use because of structural advantages over other materials. Research on metal to metal adhesives has also been successful to the point that these materials have in many cases moved from the category of secondary structure bonding to their use in primary flight vehicle structures. Further improvement in the structural capability of materials of this type is indicated and forms the basis for the current and planned materials research on nonmetallic composite materials. While this may narrow the scope to such types as reinforced plastics and high performance adhesives for bonding structural materials, it also at the same time brings in necessary consideration of many other types of materials. For instance, since reinforced plastics are actually a composite of reinforcement and binder, integrally related research effort must be expended on both the reinforcement member and the binder to obtain the highest possible improvement. A further important consideration concerns the process by which the component materials are combined into a completed structural unit, since this can have a pronounced effect upon final properties and material capability.

### Discussion

The format for the discussion to follow comprises the state of the art and research efforts according to individual material components, uses, and composite processes.

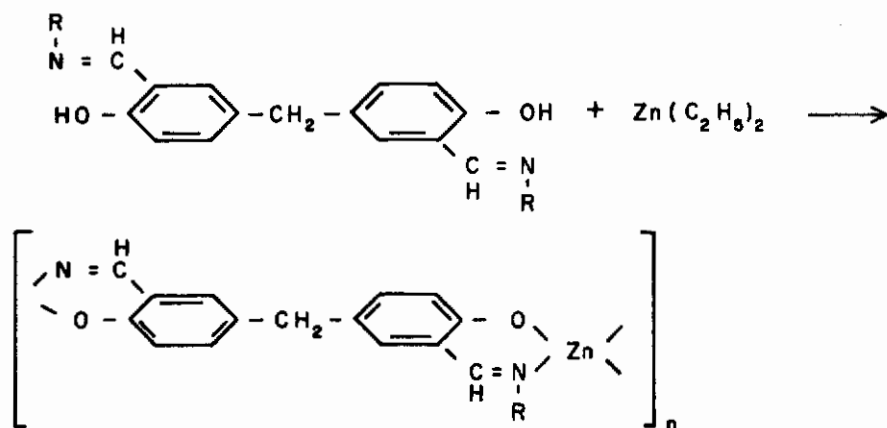
Broadened effort to obtain radically improved reinforced composites has expanded the category of materials formerly referred to as laminating resins to what may generally be called matrix materials. Laminating resins are still an important sub-category, but so are any other materials possessing the specific properties which will enable it to perform a load transfer function within the composite.

Laminating resins based upon high polymeric materials have received by far the most attention in the effort to obtain new and improved matrix materials. Progressive development has proceeded from original polyester formulations to the silicone-modified phenolic resins representing the latest completed development. While other advantageous features have been obtained such as reliability and ease of processing, the principal Air Force endeavor in all of its resin research has been directed toward improved high temperature capability. As a result of this research, the present capability in laminating resins is around 500°F for conditions of long time exposure, and up to 700°F for shorter periods of time.

Improvement beyond the 500°F temperature has been difficult for long time exposure. The silicone and silicone modified phenolic resins can provide usable strength to 700°F depending upon the time and temperature, but generally not to exceed a few hours at 700°F.

To obtain long time thermal stability at 700°F and above, new and radically different approaches must be investigated. One general approach is the utilization of unique organic, semi-organic, and inorganic polymers having outstanding thermal stability. To obtain high molecular weight polymers of these types a great deal of research is underway and will include modification of some of the advanced polymer types to provide the required mechanical and adhesion characteristics.

An example of a specific type under study is the chelate coordination polymer. Its selection was based on the observation that in many instances its coordination with metals induces temperature stability in the polymer. This has indeed been true with a polymer formed through the reaction of methylene-bis-salicylaldehyde with diethyl zinc in pyridine solvent:



However, to be useful as a laminating resin, other characteristics must be favorable. Of these, two characteristics which have not been satisfactorily achieved as yet in this type polymer are molecular weight and extensibility or toughness, and it appears that the two properties are quite closely related. Molecular weights on the order of 10,000 have been obtained. However, it has been tentatively concluded that for a polymer system containing such rigid segments a molecular weight of at least 40,000 to 60,000 must be obtained in the linear polymer, before crosslinking, to insure good mechanical toughness. Efforts at the present time are being concentrated on means of obtaining this minimum molecular weight. However it is significant that even with the low molecular weight polymer, it has been possible to prepare a reinforced laminate. The laminate is of low strength, but to our knowledge, this is the first chelate polymer from which any laminate could be prepared.

Similar efforts are underway on a borazole resin which, because of its ring structures of alternate boron and nitrogen atoms, possesses thermal stability above 800°F.

Another approach under study which may generally circumvent the low molecular weight problem of the inorganic or semi-inorganic polymers is that of converting high molecular weight organic polymers to semi-organic polymers of high molecular weight. In many heat resistant polymeric systems already available, it has been demonstrated that in most cases it is thermally weak linkages which produce premature oxidative degradation. The methylene bridges in phenolic resins are a case in point. If these



bridges can be replaced by reactive inorganic groups it may be possible to obtain high molecular weight inorganic polymers of resinous materials which will also possess good mechanical and thermal characteristics.

For extended time temperature capability above 1000°F, it is unlikely that these new polymers, if successful, will perform satisfactorily. More promising, however, is another approach under investigation which is producing some interesting results based on a system of phosphate bonded oxides or what may generally be called chemical reaction cements. The potential of such materials is very good, since by chemical reaction at low temperatures it is possible to form a matrix material thermally stable above 2000°F. This approach may appear to be quite similar to other programs on fiber reinforced ceramics. However, in ceramic materials with their very high elastic moduli and low elongation, it is not possible to realize in the composite the high tensile strength of presently available fibrous bodies. Those mentioned showed elastic moduli of less than 500,000 psi, bending strength up to 3,000 psi, and total deformation approaching 1.0 percent when tested at elevated temperatures of interest. A typical load-deformation curve and composition for one of these experimental inorganic matrix materials is shown in figure 1. Incorporation of a suitable fiber into such a matrix could provide a composite with strengths of several hundred thousand psi. Most of these acid phosphates are extremely corrosive when in contact with glass fibers, and this has prevented an early realization of such composites. Work is continuing on protective coatings from fibers and development of less corrosive matrix materials of this type.

The mention of a "suitable reinforcement" introduces another component material which is receiving vigorous and diversified research to obtain significantly improved properties in structural composites.

Recently completed research concentrated on vitreous materials which could possibly be fiberized, and an exhaustive study was made on both compositions and fiber forming techniques. Two distinct improvements were desired: (1) a significant increase in the fiber modulus of elasticity and (2) improved strength and modulus at elevated temperature.

Toward the former requirement, a successful research program provided YM 31A, which is basically a silica-based glass composition, but containing approximately 12 percent beryllium oxide. This glass can be fiberized in the same manner as conventional "E" glass, has at least equivalent strength properties and chemical resistance, and about 50 percent increase in modulus of elasticity. The improvement in fiber properties has been realized in the laminate (figures 2 and 3).

Improvement in fiber strength at elevated temperature has also been obtained to a lesser extent by several new glass compositions. The fiber tensile strength of two of these new glasses as compared to "E" glass at elevated temperatures is shown in figure 4. Further exploratory research has indicated that the elevated temperature strength may be significantly increased by both inorganic coatings on the fiber and improvement in fiber forming techniques. Studies to achieve the maximum from both of these factors are presently being conducted.

Within the last year specific programs have also started on radically new and different reinforcements for composites. The very high strength obtainable in materials of small cross-sectional area such as whiskers has been known for some time. Also, there are some materials which possess outstanding physical properties, even in bulk form, and would have very great potential if the materials could be obtained in a form suitable for composite reinforcement. Examples of such materials are beryllia, alumina, elemental

boron, and boron carbides and nitrides. Preliminary research has shown that fibrous forms can be obtained from these materials. The particular problems have been homogeneity and sufficient length. There is no theoretical reason why both of these factors cannot be achieved. Furthermore, it should be remembered that other forms of reinforcement can be utilized, such as the glass flake reinforced laminates already developed. The importance of considering a material such as boron for reinforcement is evident from its fundamental properties. Amorphous boron, for instance, with a specific gravity of 2.4, tensile strength of 350,000 psi, modulus of elasticity of  $64 \times 10^6$  psi, and a melting point of over 3600°F could provide a structural composite material with a specific modulus of 25 million psi if effectively used as a reinforcement. Also, the high modulus of elasticity of such a reinforcement will allow the use of higher modulus, very high temperature-resistant, inorganic-matrix materials of the type previously mentioned.

As noted earlier, a review of composite materials must also include consideration of the process by which the component materials are combined into the completed composite. These fabrication procedures and processes have, in general, been satisfactorily developed by straightforward engineering concepts to take best advantage of the new and improved component materials. One exception, which could contribute outstanding improvement in efficient and unique utilization of the component materials, is filament winding. This type of materials construction has the following major attributes: (1) optimum utilization of the high tensile strength of the reinforcement fibers by orientation so that the fibers carry the bulk of the stresses and (2) process and fabrication variables which can be closely controlled so that uniform and reproducible structures are obtained. The fabrication procedure is applicable to surfaces of revolution and does not complicate fabrication of even the largest structural items. The process basically involves the controlled placement of resin impregnated reinforcements under tension on a mandrel of the desired shape. The success of this fabrication procedure is largely dependent on the properties of the component materials and the process interrelationships which effect the properties of the component materials as they are applied to the mandrel.

The potential of this process has been demonstrated in the fabrication of rocket motor cases in current weapons systems when the ultimate in strength to weight properties is desired. Further research in the area of filament wound composites will provide even greater capabilities. Two of the most critical areas involve the reinforcement and matrix materials, which have already been discussed. In addition, research is required on the design of the composite structure (winding pattern or fiber orientation) and processing or fabrication techniques.

Research efforts have already been devoted toward obtaining optimum matrix materials for use on filament wound composites at temperatures of 750°F, analysis and optimization of process parameters utilized in filament winding, and obtaining meaningful procedures for defining the basic mechanical properties of filament wound composites. New epoxy-novolak resins are suitable for use at 750°F for filament-wound composites — a substantial improvement over previously available filament winding resins, which were satisfactory for temperatures up to approximately 300°F. The inherent materials and process variables were studied to determine which of these parameters are important. These were then closely analyzed and improved so that the most satisfactory filament wound composites, from a strength to weight ratio aspect, could be provided. The program provided initial data which indicated that the amount of tension, evenness of tension, and packing of the reinforcement are the most important parameters. Optimum levels for each of these parameters were ascertained and filament wound composites obtained which enabled 350,000 psi in the glass to be achieved before failure. Meaningful and reproducible



procedures for defining the significant basic mechanical properties of filament wound constructions were also obtained under this program. Optimum specimens and procedures were designed to give an accurate indication of the properties of filament wound composites. These procedures include properties such as hydrostatic burst, hoop tensile, longitudinal tensile, axial compression, interlaminar shear, and flexure. These techniques, procedures, and concepts have been obtained to solve one of the most significant problem areas presently existing in the filament wound composite area. Successful implementation of these procedures will eliminate the present confusion and lack of knowledge in regard to the properties of filament wound composites so that the designers can be provided with accurate data which can be most efficiently translated into end item design.

The successful completion of this program has clearly indicated one of the most critical problem areas, that of winding patterns. Parameters which must receive special attention are end closure design, length/diameter ratio, size and shape of openings in the pressure vessel, wall thickness/diameter ratio, longitudinal-circumferential winding vs helical winding, etc. A program is being conducted on a theoretical stress analysis and experimental data basis which will provide optimum solutions and concepts to be obtained for the highest strength to weight ratio filament wound composites. Figure 5 gives the level of properties presently being obtained with available materials and processes along with an indication of possible improvement.

The assembly of metal airframe structural components with adhesives instead of rivets, bolts, and other mechanical fasteners has many performance advantages in points of strength, stiffness, economy, weight saving, aerodynamic smoothness, fatigue resistance, and damping, as well as certain production advantages in permitting fewer parts and fewer operations.

The first design acceptance of the concept of bonding metal airframe parts together came with the advent of metal helicopter rotor blades. The lifetime of adhesive-bonded aluminum blades was increased several hundred percent over that of aluminum blades assembled with rivets, welds, and bolts. The difference was in the ability of the adhesive-bonded blades to withstand the severe fatigue caused by repetitive alternating bending moments and stresses during flight. Adhesive bonding permits the joining of areas instead of points, thus permitting a gradual transfer of the load from one member to the next by eliminating the stress risers such as the holes of bolted or riveted joints.

Further impetus to the use of adhesives came shortly thereafter with the introduction of sandwich construction which for the purposes of this discussion is defined as a low-density honeycomb-type core bonded to and between two high-density, high-strength face sheets. Sandwich constructions exhibit higher strength per weight ratios than any other type of assembly. There are no protruding rivet heads to disrupt aerodynamic smoothness. A bonded sandwich will flex or bend as a single unit. The skin is provided almost continuous support by the core cell walls.

It was largely because of the advantages offered by adhesive-bonded sandwich constructions and adhesive bonding in general that aircraft performances have advanced to the degree that they have. At the same time, however, it is ironical to note that the same high speed capabilities which these developments helped to create, through lowered weights, increased strengths, improved fatigue resistance, aerodynamic smoothness, simplified design, etc., are now imposing limitations on their continued use. Adding to the increasing temperatures imposed by aerodynamic heating at the higher speeds are the higher temperatures imposed by modern engines.

Although organic adhesives of various chemical types with heat resistant capabilities up to 300°F served well in the fabrication of aluminum airframe structures, the introduction of high performance flight vehicles and the associated increases in temperature resistance requirements have dictated the use of metals of higher and higher temperature resistance and a need for adhesives of equivalent heat resistant capabilities. While modified organic adhesives have been developed for bonding stainless steels into structural components of adequate strength for short time exposures to temperatures in the order of 500° to 600°F, the thermal capabilities of these adhesives are still far below those of the metals and appear to be nearly the ultimate that may be expected from purely organic materials. Brazing and welding have further increased operating temperatures but these are expensive and tedious operations which are difficult to control. Also, brazing alloys necessarily have softening points lower than those of the adherend metals and thus limit the thermal and strength capabilities of the structure to those of the joint. Although inorganic ceramic type adhesive-bonded joints of stainless steels have been developed capable of withstanding tensile loads of several thousand psi at temperatures up to 1000°F, they have exhibited an inherent objectionable property of brittleness. In addition, constantly changing concepts of supersonic speed and space travel are extending the elevated temperature resistance requirements beyond the capabilities of even the stainless steels, and likewise those of available adhesives, into ranges to 2500°F and above.

While nickel or cobalt based metal alloys and refractory metals hold promise of satisfying the requirements for metals of such ranges of temperature resistance, adhesives of equivalent capabilities remain to be developed. Current Air Force research programs are predominantly targeted on such objectives. That the ultimate thermal and strength properties to be expected from organic adhesives will fall short of meeting the advancing requirements seems to be evidenced by three significant facts.

First, commercial resin and adhesive manufacturers who contributed well of their skills, facilities, and capital in developing the first adhesives adopted for military use have failed to qualify a single adhesive under a now 6-year old specification. The principal target requirement of 1000 psi tensile lap-shear strength at 500°F after 192 hours exposure to 500°F in itself is but a token requirement in comparison to the existing and future requirements for stable bonding materials at temperatures upward to 2500°F and for longer periods of time.

Second, although contractual programs for modifying organic adhesives with inorganic additions have succeeded in extending the 8-day thermal stability to 600°F, the resultant initial and elevated temperature strengths have been materially reduced. The first best so-modified adhesive was an epoxide-phenolic resin based adhesive, modified with a silicone resin. Although the silicone resin contributed to the thermal stability of the composite adhesive, the thermoplastic property of silicones in general was reflected in substantially reduced strength of the composite bond at elevated temperatures. Further but still limited progress was made in a research program based on the heat stabilizing effects of various metallic oxides on organic resins. Since organic adhesives of normally poor elevated temperature strengths were found to retain substantial percentages of their room temperature strengths even at elevated temperatures if heated in an inert nonoxidizing atmosphere such as nitrogen, it was theorized that the addition of antioxidants to the adhesives would respond in like manner. This program resulted in an adhesive which displayed a tensile lap-shear strength of 1000 psi at 600°F after 10 minutes exposure to 600°F and 750 psi at 600°F after 8 days of exposure at 600°F. This was an epoxy novolac modified silicone-phenolic heat stabilized with arsenic pentoxide. The state of the art for organic adhesives, in view of these recent developments, can be summarized as shown on the next two figures (figures 6 and 7).



Also, although programs of basic research to synthesize new chemical types of thermally stable organic resins specifically for use in structural metal to metal adhesives have succeeded to the extent of producing resins having in themselves high softening points (above 700°F), to date adhesives based thereon have exhibited poor mechanical strength even to exposures of only 400°F, even though displaying acceptable strengths at room temperature. The most promising candidate materials in these investigations have been polyisocyanurate polymers in which the heterocyclic ring consists of alternate carbon and nitrogen atoms. Investigations to improve the adhesive and elevated temperature strength properties of these polymers are based on the incorporation of controlled amounts of free isocyanate groups in the polyisocyanurate molecule and by attaching phenolic groups to the polymer chain. Progress in this field has however not been particularly significant.

In realization of the obvious impending need for structural adhesive systems capable of bridging the gap between the limited thermal properties of organic materials and the higher thermal capabilities of structural metals other than aluminum, early attention was focused on vitreous and ceramic materials. Based on certain available background information in the field of vitreous enamels and porcelains, preliminary investigations were centered on three general types of compositions, the ceramic-oxide glassy-bonds, the cermets, and the air-setting varieties. The glassy-bond types were found to be superior to the others, particularly in such properties as elevated temperature stability, adhesive strength, low moisture sensitivity, and suitable firing and maturing temperatures, as related to the heat-treating requirements and thermal expansion properties of the adherend metals, and have been the basic structure in succeeding investigations.

A relatively simple ceramic-oxide type adhesive frit is one composed of silicon dioxide, sodium monoxide, and boron oxide obtained by melting together, respectively, raw quartz, sodium nitrate, and boric acid, quenching the resultant molten glass into water (which shatters it and makes it easier to grind in a subsequent ball-milling operation), drying, and then milling to a desired fineness. Each of the above oxide-frit components contributes a particular property to the resultant adhesive--thermal stability by the silica, wetting of the adherend metal by the boron oxide, and thermal expansion control by the sodium oxide. Actual application of the dried and ground frit as an adhesive is accomplished as a slip or slurry obtained by milling the frit with water and usually a suspension agent, such as colloidal silica, to a desired consistency, for brush, dip, or spray application to the faying surfaces, and then firing the assembly at specific temperatures, pressures, and times. Although relatively early progress was made in effecting lap-joint bonds of stainless steels of lower ranges of temperature stability, adaptation to the higher range steels and super alloys and refractory metals, and to sandwich construction type bonding has necessitated wide-scale reformulation and reprocessing and a need for new concepts and approaches.

Initial improvements in lap-shear and lap-bend strengths were effected by placing thin metal screens in the bond line, similar to the concept used in reinforcing organic resins with fiberglass cloth. This, however, was not adaptable to sandwich panel constructions because of the difficulty experienced in inserting and maintaining the screen between the coated face sheets and the honeycomb core throughout the firing and maturing cycles. Although additions of fine powder carbonyl iron also made for stronger lap-joints, these additions promoted excessive localized oxidation of the core when applied to sandwich-construction bonding. In like manner, while additions of aluminum oxide promoted increased lap-joint strengths, particularly lap-bend strengths, principally because they imparted greater porosity and therefore greater flexibility to the bond, this porosity was undesirable in attempting to effect a good bond with the thin foil edges, or feet, of the cores in sandwich type constructions.



Probably the most significant of the continuing improvements in the development of ceramic adhesives for metals has been motivated by a concept previously substantiated in the field of porcelain enamels. This is based on the premise that improved adherence between a glass and a metal and improved wetting of the metal surfaces are obtained if the glass contains the oxide of that metal. Relatively easy confirmation of this concept and its possible applicability to ceramic adhesives was obtained with additions of small quantities of ferric oxide to a typical silica-sodium oxide-boron oxide slip which resulted in markedly improved strengths in bonds to steel. Likewise, additions of nickel and cobalt oxides to ceramic-oxide frits have improved strengths of such adhesives when used to bond such nickel and/or cobalt based alloys as Inconel X and Rene' 41. Further strength improvements have been promoted by further applying this principal to the extent of flame spraying a thin film of nickel-chrome alloy to the faying surfaces as part of the surface cleaning treatment prior to adhesive application. Additions of powders of the individual representative adherend alloy metals themselves as well as their oxides, to the ceramic frits and/or slips have also improved bond properties. Powders of the alloyed metals themselves have further contributed. Additions of oxides of metals other than the base metals of a given adherend metal alloy, for instance chromium, appearing in the adherend metal alloy, even though in relatively small percentages, have also contributed to the over-all improvements in strength and thermal stability of the ceramic bonds. Even metals and oxides thereof not even represented in the base adherend metals, for instance zinc and copper, have also contributed in certain measure depending on how incorporated and in what proportions. Eutectic mixtures are not necessarily the best mixtures. The pattern of obtaining an optimum formulation appears to be one of statistical analyses of many candidate materials and possible combinations. The pattern of bonding seems to be approaching that of a brazed joint to the extent of establishing a continuous metal phase. However, increased thermal stability is being realized and the objectionable properties of brittleness and frangibility inherent in glassy bonds are being reduced by these developments. Further progress in these respects is expected from current studies on recrystallized frits, annealed bonds, and bonding mechanism studies.

Feasibility of bonding refractory metal to refractory metal using ceramic bonds has also been demonstrated. These investigations have to a marked degree followed the same approaches used in the work with the lower temperature range metals, - that is, developing a basic glassy frit and introducing the oxide of the particular base refractory adherend metal and other oxides of high melting temperatures. Best bonds whether of tungsten to tungsten, molybdenum to molybdenum, tantalum to tantalum, or columbium to columbium, have been effected where tantalum pentoxide replaced the silica as the primary glass forming agent.

Another current program of work is based on a novel approach involving the use of metal brazing alloy foils in conjunction with vitreous compounds in order to incorporate the favorable characteristics of both materials, the ductility and strength of the braze and the thermal stability of the ceramic. Although the feasibility of this approach has already been substantiated by impressive lap-shear strength data obtained on bonds of various stainless steels, the major objectives of the program are the examination and determination of the mechanism of the interaction between the braze and the ceramic, and in turn the adherend metal, and the examination and determination of the physical and chemical structures of the resultant bonds. Based on initial findings to be determined with stainless steel adherends, it is proposed to further synthesize and formulate ceramic-braze combinations specifically adaptable to bonds of adherend metals of still higher thermal stability such as the nickel or cobalt based super alloys and the refractory metals. X-ray and photomicrograph studies are intended to establish the optimum compatibilities of the candidate materials with radioactive tracer techniques being

employed to establish the mechanism and structure of the bonds. The expected levels of strength for these various approaches to inorganic bonding is shown in figure 8.

Another unique method for joining metals has recently been successfully adapted to the fabrication of metal sandwich constructions.

This method, for which patent applications have been initiated, has been termed the exo-flux method wherein the prefix "exo" refers to an exothermic-reactant composition which, when applied to, and ignited on, the external surfaces of the metals to be joined, imparts an intense instant heat of short, flash duration to a metal oxide "fluxing" agent and element metal donating material which has been placed within the bondline (on the metal faces to be joined) and forms a strong adhesive joint with a continuous metal phase. Under these spontaneous conditions of firing, the metal oxide of the fluxing agent releases its metallic portion to form a eutectic with part of the base adherend metal. Although to date formulations and techniques have been proportioned specifically only for bonds of stainless steels, effective bonds have been made with most of the heat-treatable stainless steels, including 17-7PH, PH15-7 Mo, AM-350, AM-355, A-286, -302, and -321, giving promise that the process may be adaptable also to the bonding of higher temperature resistant alloys such as Inconel X and Rene' 41, and perhaps even the refractory metals (tungsten, tantalum, molybdenum, etc.).

A significant point for the exo-flux method of joining is that it adds relatively negligible weight to a structure so bonded as evidenced by a comparison of the 0.3 lb. per sq. ft. general average of brazing alloy required to effect a brazed sandwich panel and the 0.006 lb. per sq. ft. of exo-flux required to effect the same panel.

Although, as stated, major emphasis is being placed on elevated temperature resistant inorganic type adhesives, two other programs of endeavor in the field of adhesives are worthy of mention even though they are of a "specialized" nature and tied to the lower temperature range organic types. In brief review these are:

1. Room temperature curing adhesives have been in continuing need for field and emergency repair of aircraft where the pressurizing and heating equipment normally required for curing are not available. A two-part, low-pressure, ambient-temperature curing adhesive system based on an amine-cured novolac epoxy resin has been developed which meets prime target strength and pot life requirements. A formulation concept of using metallic chromates as filler materials proved to be a simple yet effective means of overcoming a general susceptibility of epoxy-resin-based adhesives to salt spray and humidity exposures, which susceptibility had also plagued prior endeavors with acrylic and resorcinol type resins.

2. As needs for adhesives of increasingly high temperature resistance have been growing, so also are requirements for adhesives which will resist cryogenic temperatures. This does not imply that both properties must be possessed by any one adhesive--composite construction designs being such that although both conditions of temperature extremes would be encountered within an over-all structure, they will be confined to separated components insulated from each other. Preliminary studies on commercially available organic adhesives of representative chemical types indicate that further development of cryogenic adhesives can be made in the field of organic materials. The preliminary evaluations were limited in scope and, accordingly, other than pointing up a preference for epoxy type adhesives over other chemical types, particularly the vinyls and phenolics, gave no indication of the capabilities of the adhesives under long time exposures, under stressed vs unstressed conditions, in bonds with various different



types of adherend metals, etc. Continuing investigations are designed to establish these and other capabilities and will include formulating to specific end-use requirements if necessary.

## Summary

In summary, it is estimated at this time that to satisfy predicted requirements and make available for use the best possible structural plastics and adhesives, research in the following areas must be continued (figure 9):

- a. Matrix materials, both organic and inorganic types, for short and long time use over the temperature range of 500° to 2000°F. Additional specific requirements in this area can be added, such as resins which are particularly suited to filament winding, and inorganic matrix with increased elongation and strength.
- b. New and improved composite reinforcements, including higher strength fibers, higher modulus fibers, and higher temperature resistant fibers, also having low density.
- c. Adhesives with increased temperature capability both for long time use in the temperature range of 500° to 800°F and short times to 2000°F. This includes adhesives suitable for use with super alloys and refractory metals.
- d. Research in the area of fabrication processes, such as filament winding, to achieve maximum obtainable properties with available materials.

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# APPARENT DEFORMATION BEHAVIOR OF SPECIMEN IN FLEXURE AT 800 °F

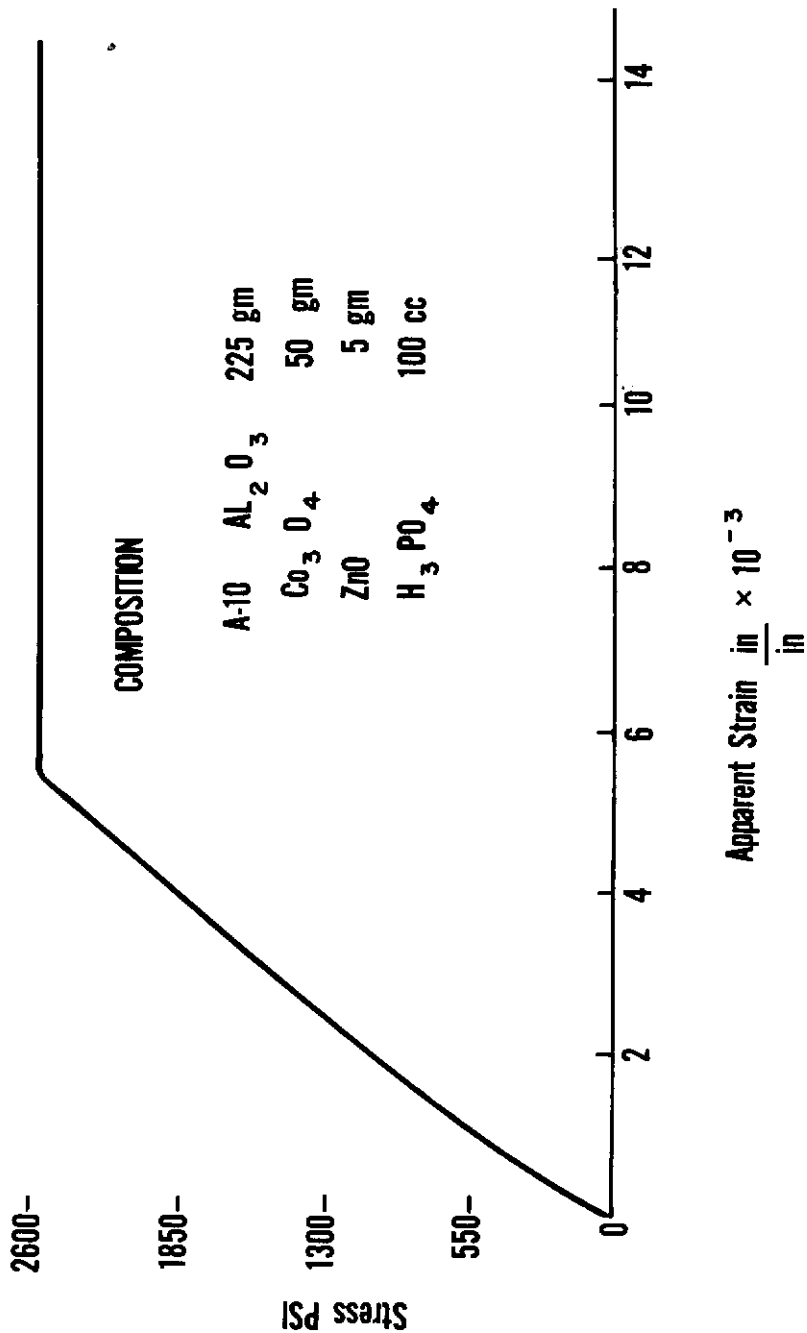


Figure 1. Load-Deformation Curve and Composition of Inorganic Matrix Material

# STRENGTH PROPERTIES OF YM31A COMPARED TO 'E' GLASS REINFORCED PLASTICS

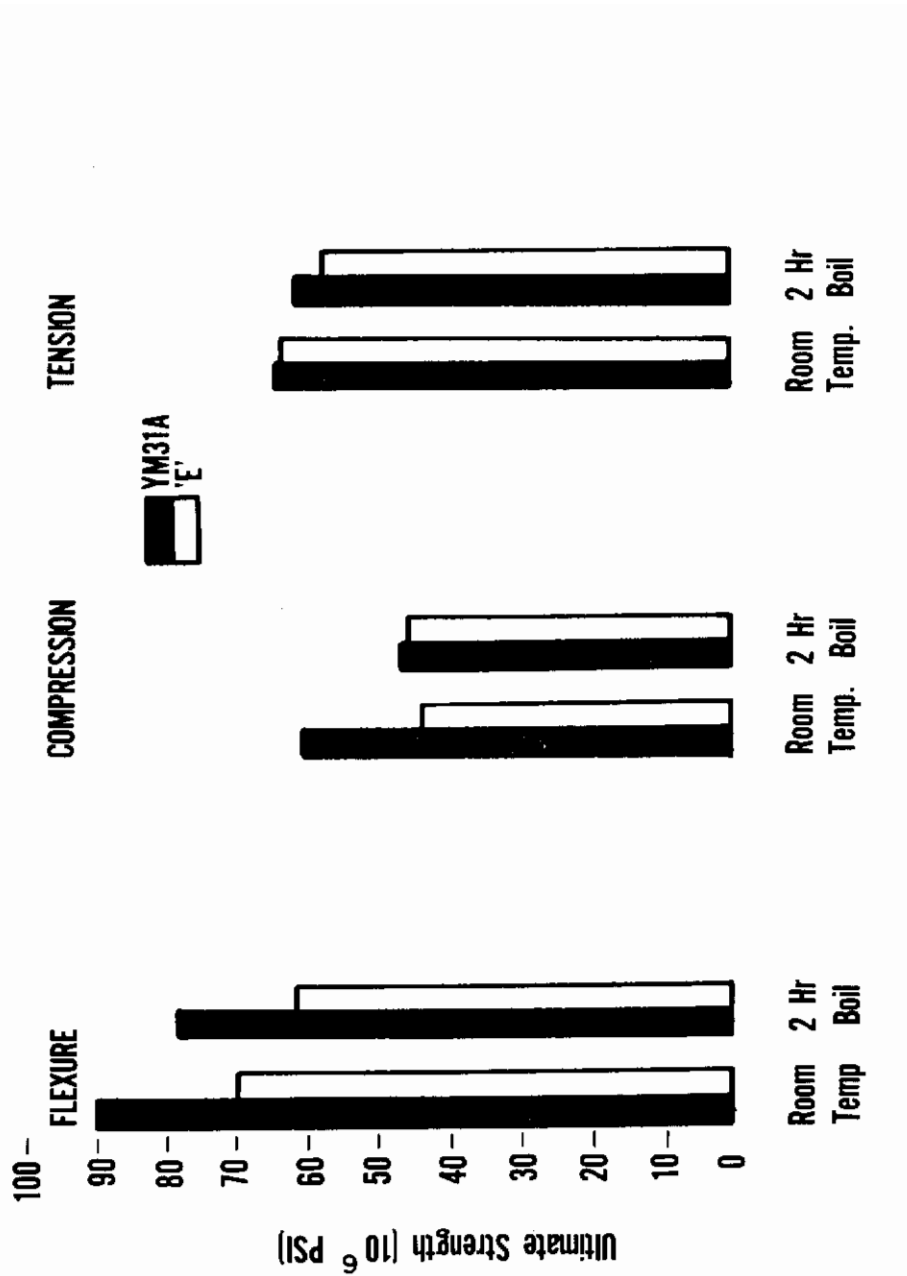


Figure 2. Strength Properties of YM31A Compared to 'E' Glass Reinforced Plastics



# MODULUS PROPERTIES OF YM31A COMPARED TO 'E' GLASS REINFORCED PLASTICS

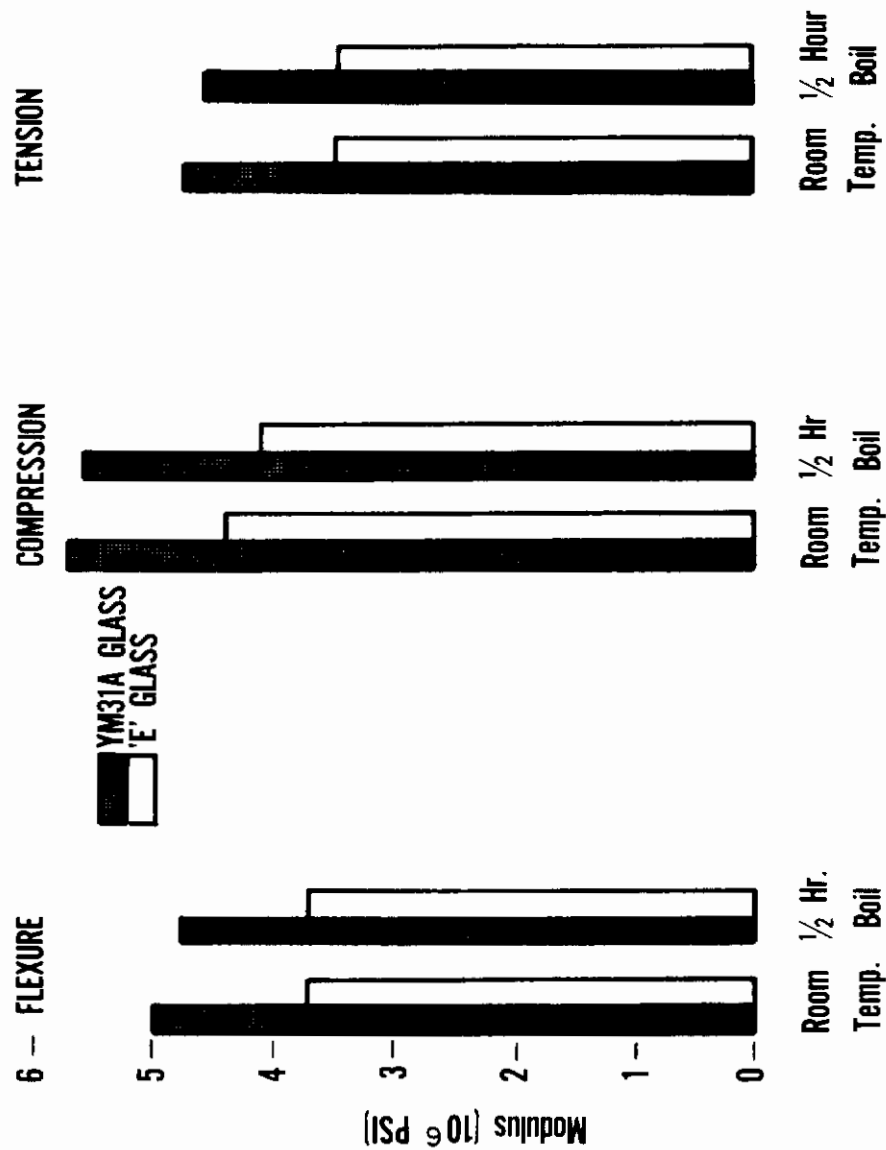


Figure 3. Modulus Properties of YM31A Compared to "E" Glass Reinforced Plastics

# STRENGTH OF GLASS FIBERS AT ELEVATED TEMPERATURES

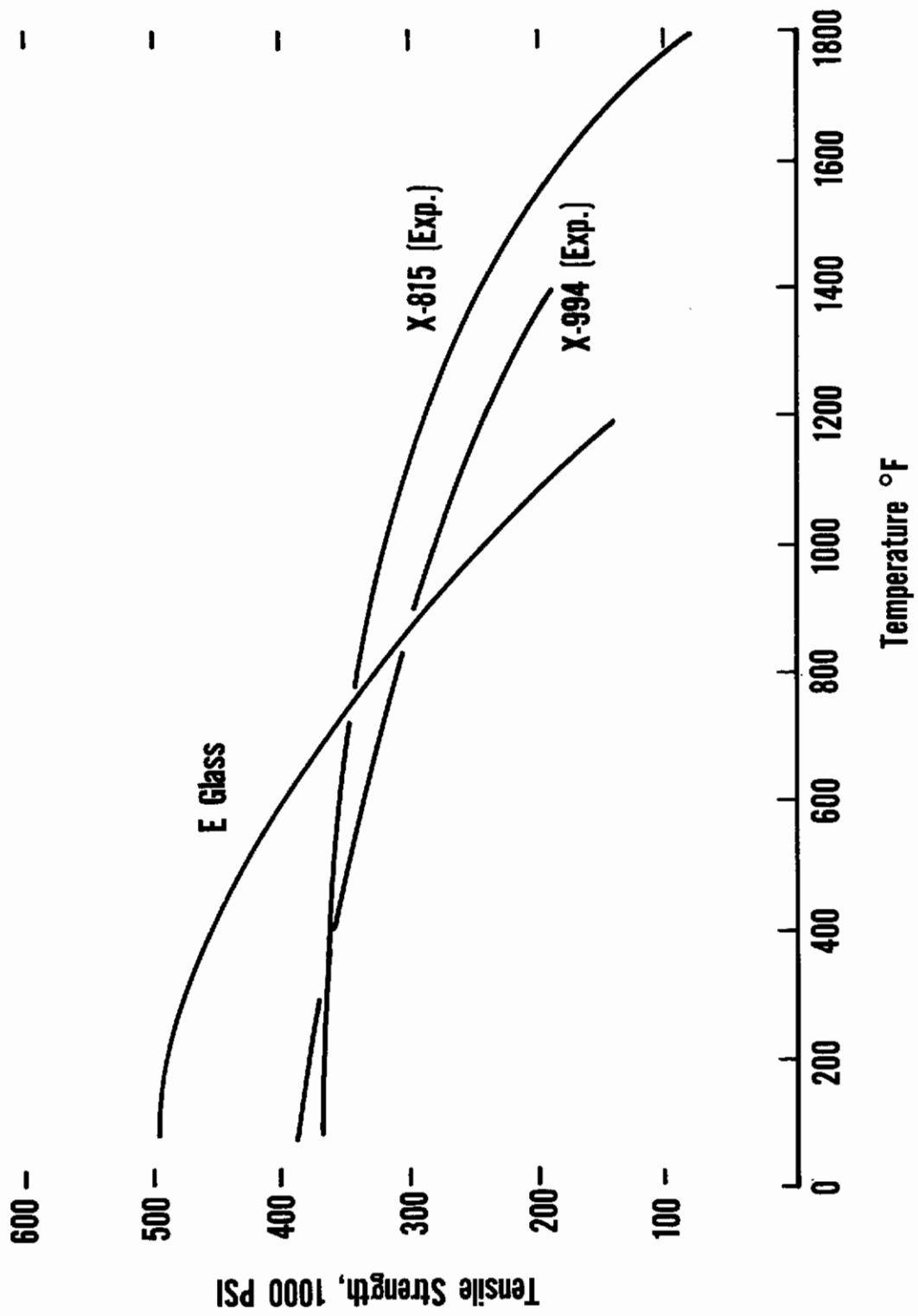


Figure 4. Strength of Glass Fibers at Elevated Temperatures

# PROPERTIES OF SOME PRESENTLY AVAILABLE STRUCTURAL MATERIALS

	Glass Fiber—Resin Filament Wound	Steel	Titanium
Density(lb./in <sup>3</sup> )	0.075 0.080	0.285	0.163
T.Y.S., psi	250,000 (Unidirectional) 225,000	220,000	150,000
Strength/Density in. x 10 <sup>4</sup>	193 160	78	92
Modulus of Elasticity, psi x 10 <sup>6</sup>	5 8.5	30	16

Figure 5. Strength Levels of Currently Available and Experimental Filament Wound Composites



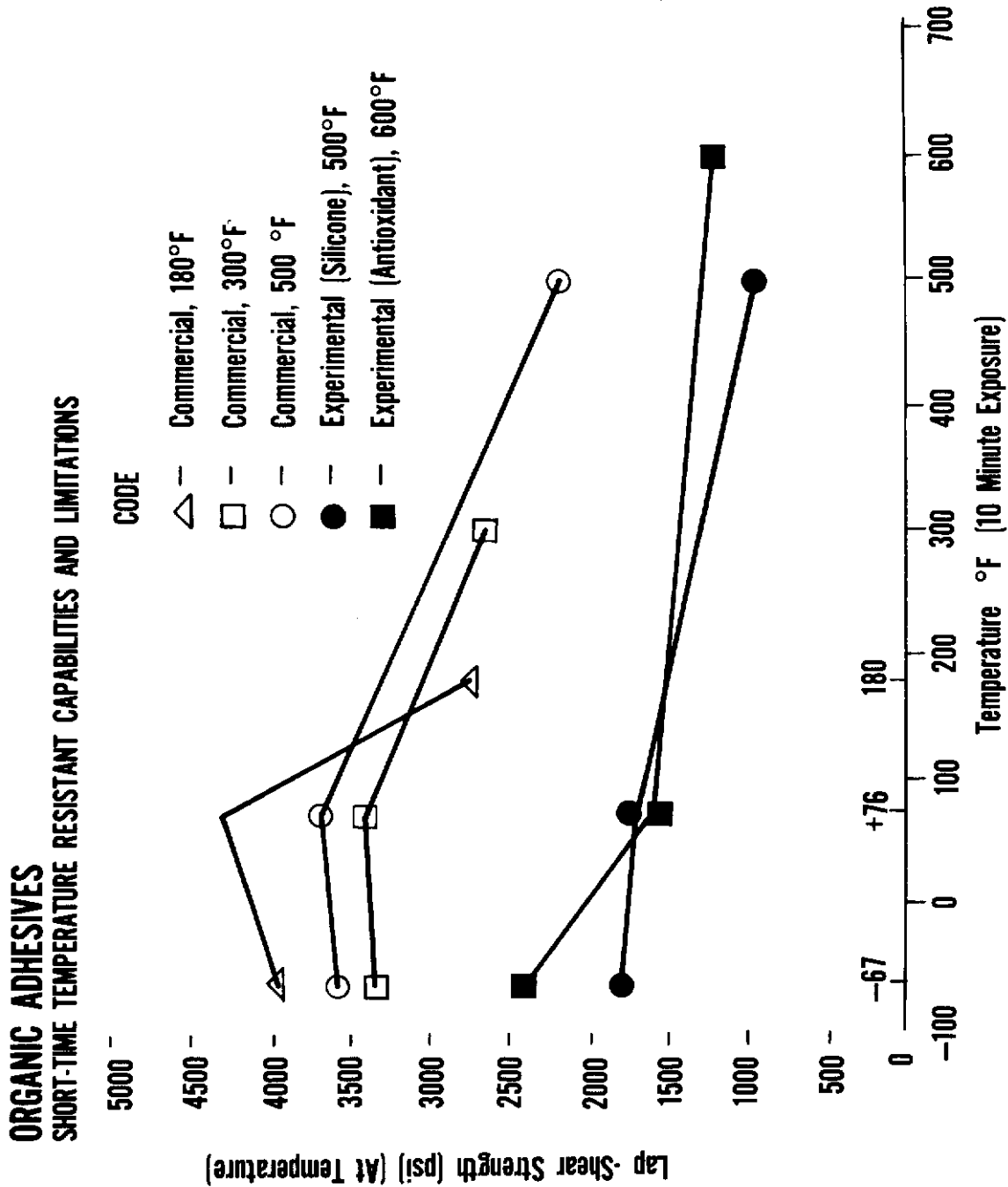


Figure 6. Organic Adhesive Bond Strengths—Short Time at Temperature

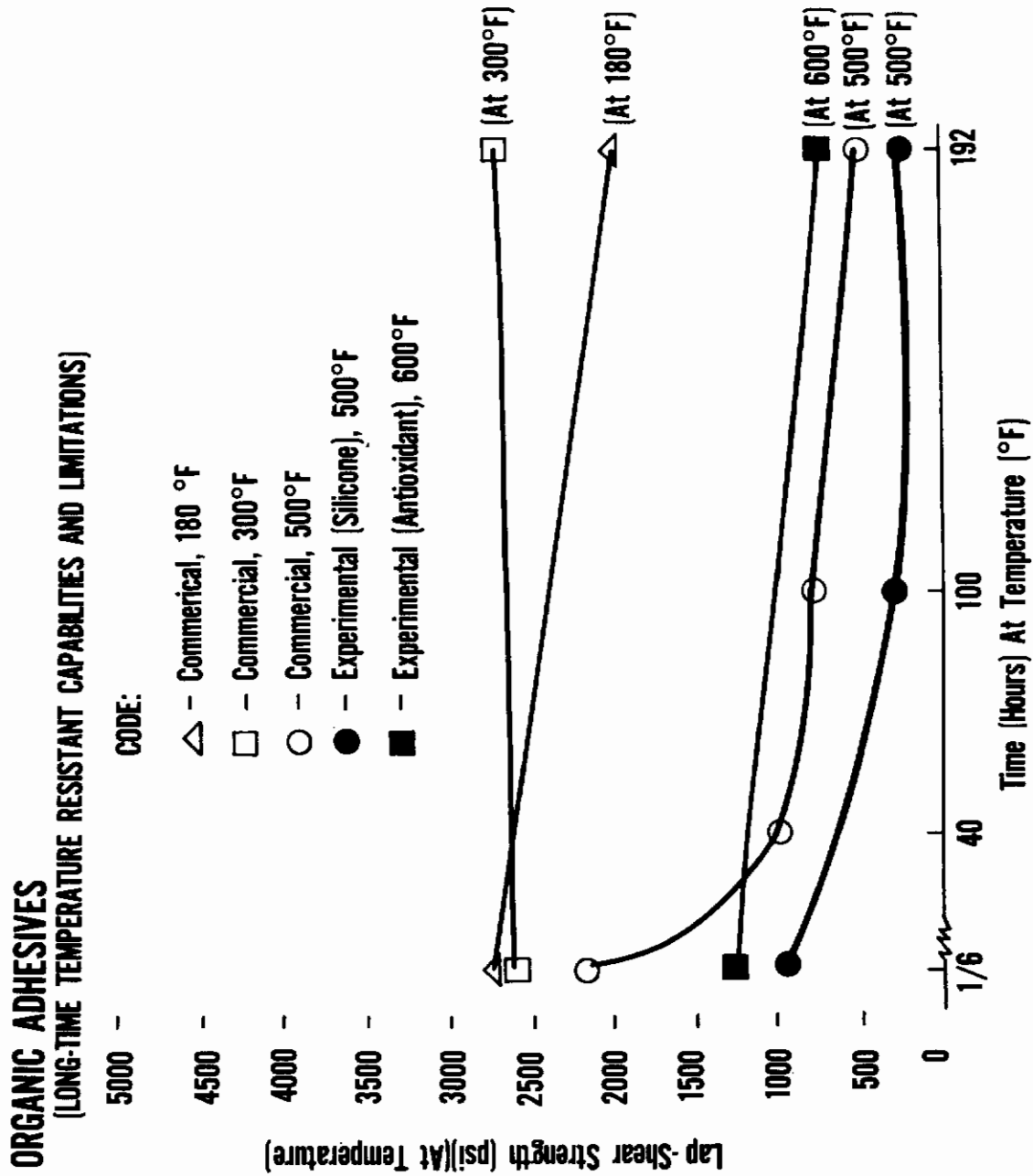


Figure 7. Organic Adhesive Bond Strengths—Long Time at Temperature

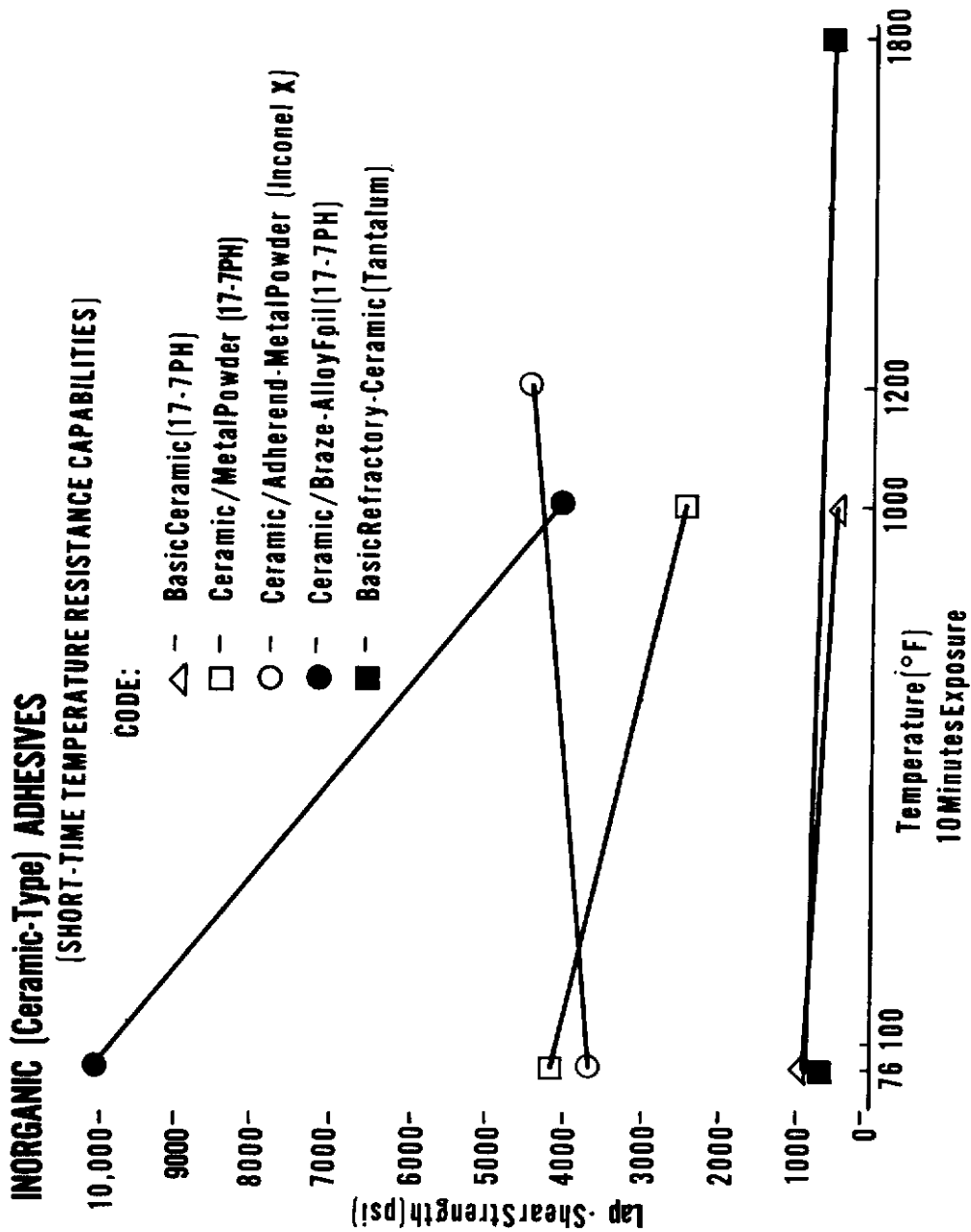


Figure 8. Inorganic Adhesive Bond Strengths—Short Time at Temperature



**DESIRED MATERIALS RESEARCH FOR  
IMPROVED NONMETALLIC STRUCTURAL COMPOSITES**

**MATRIX MATERIALS**

Organic  
Inorganic

**REINFORCEMENTS**

High Strength  
High Modulus  
High Temperature

**ADHESIVES**

Improved Temperature Resistance  
Improved Strength

**FABRICATION PROCESSES**

Figure 9. Desired Materials Research for Improved Nonmetallic Structural Composites

*Contrails*