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POLYIMIDES: THERMALLY STABLE AEROSPACE POLYMERS

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Over the past fifteen years, the government-aerospace community has spawned and proliferated materials research at an enormous rate toward achieving higher and higher levels of thermal performance. Of the many polymers that have been synthesized and scrutinized during this time frame, the aromatic polyimides have withstood the test of time. Due to their outstanding thermal stability, polyimides are presently under careful consideration for use as matrix resins, adhesives, films and coatings. If successful, this unique class of polymers could greatly extend the present 450-478K (350-400F) limit set by baseline epoxies to higher temperatures and provide longer life at higher temperatures. The U. S. Government agencies which have formed a copartnership to sponsor the development and fabrication of superior materials for airborne systems include the Air Force (Materials, Aero Propulsion, and Flight Dynamics Laboratories), the Navy (Naval Air Systems Command), and the National Aeronautics and Space Administration (NASA-Ames, NASA-Lewis, and NASA-Langley).

Polyimides have developed to the point where they are attractive for use on a variety of structures that operate at elevated temperatures such as those shown in Fig. 1. The expected service life for such applications ranges from the single flight of a missile lasting only a few minutes to the supersonic transport which will probably be used for at least 50,000 hours.

The development of polyimides to this date has been an ever-changing one. Linear condensation polyimides were originally geared toward meeting the exotic thermal needs of future aircraft, spacecraft, and missile thermal protection. Cost was a minor factor; and processing was difficult compared to that of more conventional plastics. Linear polyimides are still inconvenient to process because the soluble polyamide acid precursor must be dissolved in a solvent with a high boiling point. Conversion to the polyimide requires the elimination of water; and further curing is usually needed to remove residual solvent. Such a cure cycle makes the molding of void-free laminates tedious to say the least. Attempts have been made in recent years to circumvent the processing difficulties associated with linear polyimides by using lower molecular weight "addition" polyimides. Much has been gained in the way of processability by placing reactive elements such as olefinic end groups on short polyimide precursors allowing polymerization to take place by addition. However, the price that must be paid is a slight loss in thermal stability.

Both high-temperature linear and addition-type polyimides are available in a variety of commercial forms. Some of the more well-established polyimide resins include DuPont's Pyralin* and Kapton series of films, Upjohn-2080, Monsanto's Skybond-700 series of modified polyimides, Hexcel's F-178, Rhodia's Kerimid, and Thermid-600 produced by Gulf Oil Chemicals. More recently commercialized are the DuPont NR-150 series of polyimides, PMR-15 (Polymerization of Monomeric Reactants) resins from NASA-Lewis Research Center, and LARC-160 originating from NASA-Langley Research Center. The Materials Division at NASA-Langley is conducting both contractual and in-house research involving aromatic polyimides. Several of the current aerospace programs are aimed at the development of polyimides for applications such as composite matrix materials, structural adhesives, films and coatings.

COMPOSITE MATRIX MATERIALS

Carbon fiber composites are stiffer and stronger for a given mass than any other materials (Shell Polymers 3 No. 2 [1979] 48). For high-temperature structural applications, graphite/polyimide (Gr/PI) composites can have significantly less mass than equivalent structures of metal or graphite/epoxy composite. As the necessity to conserve fuel grows, weight-savings on future aircraft and spacecraft will become imperative.

NASA-Langley is currently directing studies toward manufacturing Gr/PI composite structures that will provide both weight-savings and potential operational capability up to 589K (600F). Under the Supersonic Cruise Research (SCR) Program, a procedure is being

* Use of trade names or names of manufacturers in this report does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

developed for the manufacture of Gr/PI wing panels for high-performance aircraft. Such panels will be evaluated in flight by installing them on the upper surface of the wing of a YF-12 airplane shown in Fig. 2. This area of the wing surface is heated aerodynamically to temperatures of 524K (485F) when the aircraft is flown at three times the speed of sound. The panels have performed satisfactorily, carrying design loads and surviving elevated temperatures. The Gr/PI panels were also 50% lighter than the titanium panels they replaced.

In a concurrent program called CASTS (Composites for Advanced Space Transportation Systems), NASA researchers are screening polyimide composite and adhesive resins for the best combination of properties for 589K (600F) service. In order to demonstrate Gr/PI technology, construction of a segment of the aft body flap of the Space Shuttle Orbiter is under consideration for ground testing. The aft body flap, however, is only one of many parts of the Shuttle that are candidates for graphite reinforced polyimide composites.

As a replacement for aluminum on large space structures, polyimides are just entering the limelight. For example, Gr/PI composites are being considered for use in structural members for very large communications platforms (Fig. 3). Polyimide composites show excellent potential for applications in space because they provide the following:

(1) Light weight and structural sturdiness

(2) A low coefficient of thermal expansion

(3) Radiation resistance superior to other materials

Four polyimide matrix resins which have performed successfully in the above programs are NR-150-B2, Thermid-600, PMR-15 and LARC-160. DuPont NR-150-B2 is a linear condensation polyimide based on the 6F perfluorinated dianhydride monomer and is noted for its outstanding thermooxidative stability. Thermid-600, originally prepared by Hughes Aircraft as HR-600, is a promising addition polyimide containing reactive acetylene groups. PMR-15 developed by NASA-Lewis is a mixture of monomers (methylene-dianiline and the esters of nadic anhydride and benzophenone tetracarboxylic acid dianhydride) in methanol.

The PMR approach has resulted in a highly processable resin which can be compression or autoclave molded. Gr/PMR-15 composites are already being used in several diverse structural applications such as the inner cowl of an experimental turbofan engine and the compressor blades for a supersonic wind tunnel. The newest of the four resins is NASA-Langley's LARC-160. Like PMR-15, LARC-160 is an addition polyimide material produced as a monomeric mixture, but is based on the low-cost polyamine shown in Fig. 4. The unique feature offered by LARC-160 is that it is an essentially "solventless" liquid resin which yields solventless drapable pre-preg with good formability. Its liquid nature allows LARC-160 to be processed by hot-melt coating and cured in an autoclave. In all probability, these four composite matrix resins will be desirable candidates for future aerospace applications.

STRUCTURAL ADHESIVES

As has been the case in other areas of technology, the development of appropriate adhesives is lagging behind the production of structural aerospace materials. In an effort to push forward structural adhesive technology, NASA-Langley has recently begun a program with Boeing Aerospace to evaluate adhesives for 50,000 hours service at 505K (450F) for supersonic cruise aircraft applications. The program will involve the screening of adhesive resins, cure cycle optimization, thermal and environmental aging of bonded titanium specimens, and the large-area bonding of a 1.22m x 1.22m titanium panel as a final demonstration article. Three out of four adhesive contenders in this program are aromatic polyimides - NR-150-B2, FM-34 (American Cyanamid), HR-602 (Hughes Aircraft), and LARC-13 (NASA-Langley).

LARC-13 is an experimental addition-curing resin, which has demonstrated good high-temperature strengths and desirable modes of failure. The success of this adhesive can be attributed in part to the unique meta-linked diamine from which it is prepared (Fig. 5). According to work reported by Boeing, LARC-13 does not blister or crack upon thermal exposure and is easy to process.

In addition to bonding titanium, steel, and aluminum, LARC-13 has shown exceptional adherence to Gr/PI composites. It is being used as an adhesive in the SCR program for bonding Gr/PMR-15 and Gr/LARC-160 composite face sheets to a polyimide honeycomb core.

The bonding of large areas with linear condensation polyimides will be difficult because a thorough release of volatiles is required to produce void-free bonds. On the other hand, a linear polymer would provide better peel strength than the highly cross-linked addition polyimides. Success will depend upon which system can offer the best combination of properties for a particular application.

FILMS AND COATINGS

Linear aromatic polyimides are choice materials for aerospace films and coatings applications. They possess a winning combination of properties which include: toughness and flexibility, remarkable thermal stability, radiation and solvent resistance, and excellent mechanical and electrical properties over a wide temperature range.

NASA recently expressed an urgent need for polyimide film measuring 2.00 μm (.08 mil) for the proposed Solar Sail Program. A spinning sail, such as the one conceived by an artist in Fig. 6, was originally intended for a rendezvous mission with Halley's Comet in 1986, following a November 1981 launch. The blades on this sail were to be 8m wide and 7350m long. Before the program was canceled, DuPont successfully produced large sheets of Kapton H-film measuring 2.50 μm

(.10 mil) in thickness. A linear polyimide film adhesive was developed at NASA-Langley for joining strips of the ultra-thin film to produce the very large blade structure. Though this program was of short duration, it was successful in greatly advancing polyimide film technology for use on future large space structures.

Polyimide film has also been contemplated for use in insulating high-temperature aerospace wires and cables. Due to its inherently low electrical conductivity, polyimide film can provide as much as 50% weight-savings and 25% volume-savings over more common insulating materials. However, for certain other space applications, a polyimide with high electrical conductivity is desirable. NASA-Langley is currently engaged in a study to incorporate metal ions into polyimides to improve the electrical conductivity of films for the purpose of relieving space-charging effects. To date, the addition of palladium chloride complexes has dramatically increased the conductivities of polyimide film from 10^{-17} to 10^{-7} $ohms^{-1}$-cm^{-1}.

The properties which make linear polyimides useful as films also make them attractive as coatings for large space structural members. A polyimide coating could potentially protect thin composite materials in space by absorbing proton radiation and thereby preserve the mechanical properties of the underlying structure. Such coatings are estimated to absorb 90% of harmful proton radiation and prevent damage from ultraviolet rays.

FUTURE DEVELOPMENTS

At this stage in development, the outlook for polyimides is bright. However, the 1980's could deliver several foreseeable demands that might deter the progress of these polymers.

The successful exploitation of polyimide composites and adhesives for aerospace applications will probably require an improvement in toughness, especially for the addition polyimides which tend to be brittle by nature. Not only will thermal stability and long-term durability be required of future materials, but also good peel strength, impact strength, and resistance to crack propagation. Research is already underway at NASA-Langley to improve the toughness of polyimide resins. The results of some preliminary attempts at combining polyimides with silicone elastomers are given in Fig. 7. This branch of polyimide research is new, and presents many appealing challenges to find higher temperature elastomers, to gain compatibility between the rubber and polyimide, and to search for better methods of testing.

At the start of the next decade, the aerospace industry as well as the auto industry will probably be taking a more serious look at polyimides as replacements for epoxies in graphite reinforced composites. In addition to replacing the epoxy matrix, NASA-Langley is considering polyimide fibers as potential replacements for graphite fibers in composites of the future. Though the search is in its earliest stages, polyimide fibers have already been spun from solutions of liquid-crystalline polyamide acids. Polyimide/polyimide composites would potentially offer: (1) better compatibility between the resin and fibers and (2) weight-savings due to a lower density fiber.

Future endeavors will be directed toward reducing the cost of those polyimides already in the marketplace. Polyimides currently bear the same stigma of high cost that is usually associated with low-volume, high-performance specialty items. The synthetic chemist and process engineers face an important challenge to reduce the high cost of monomers and polymerization processes for both existing and experimental materials. Though polyimides were carried through the past decade on the laurels of their outstanding thermal stability, future years may force upon them and other polymers critical new demands, some of which are yet to be conceived.

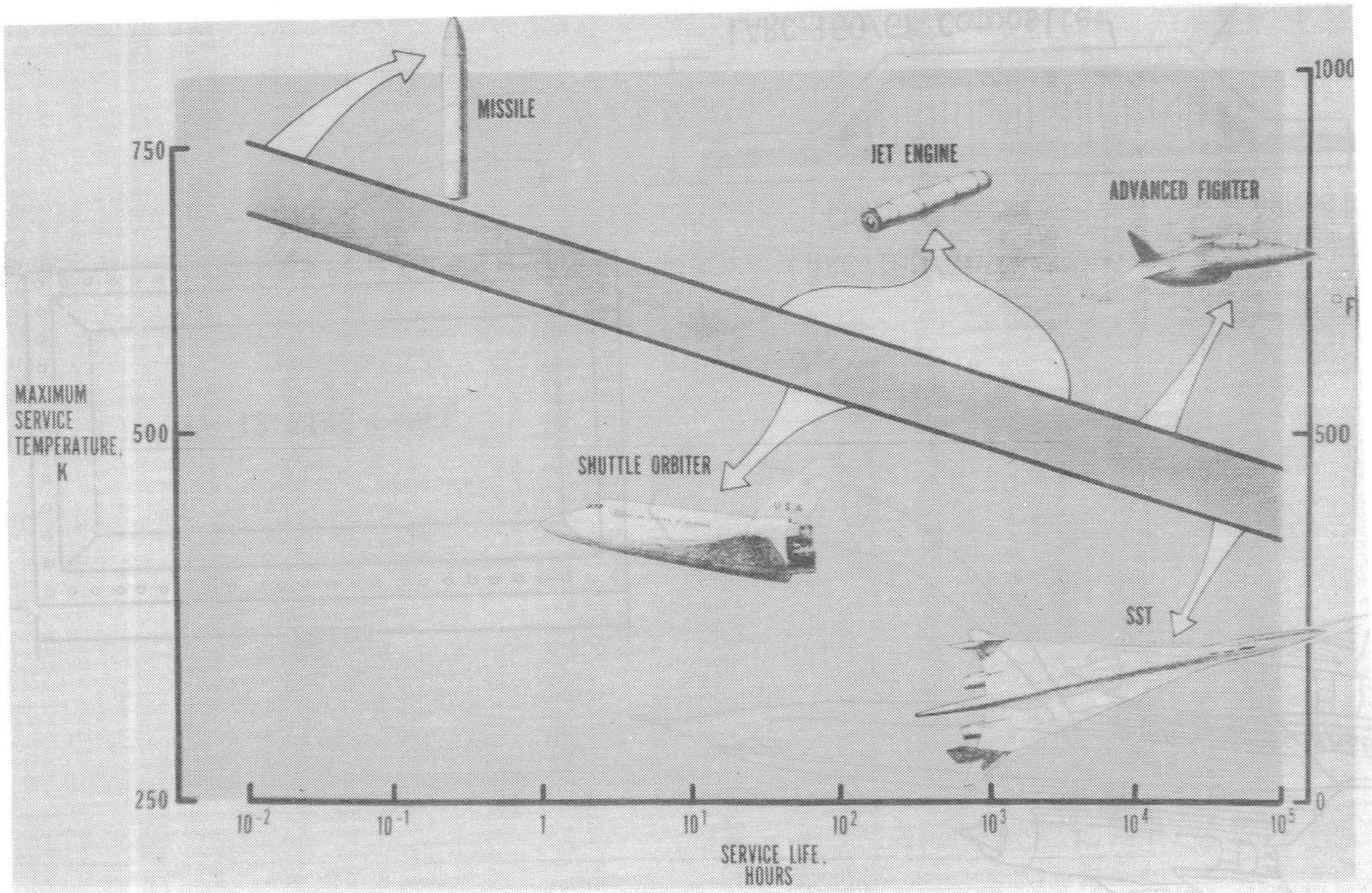

Figure 1. Time-temperature capabilities of graphite/polyimides.

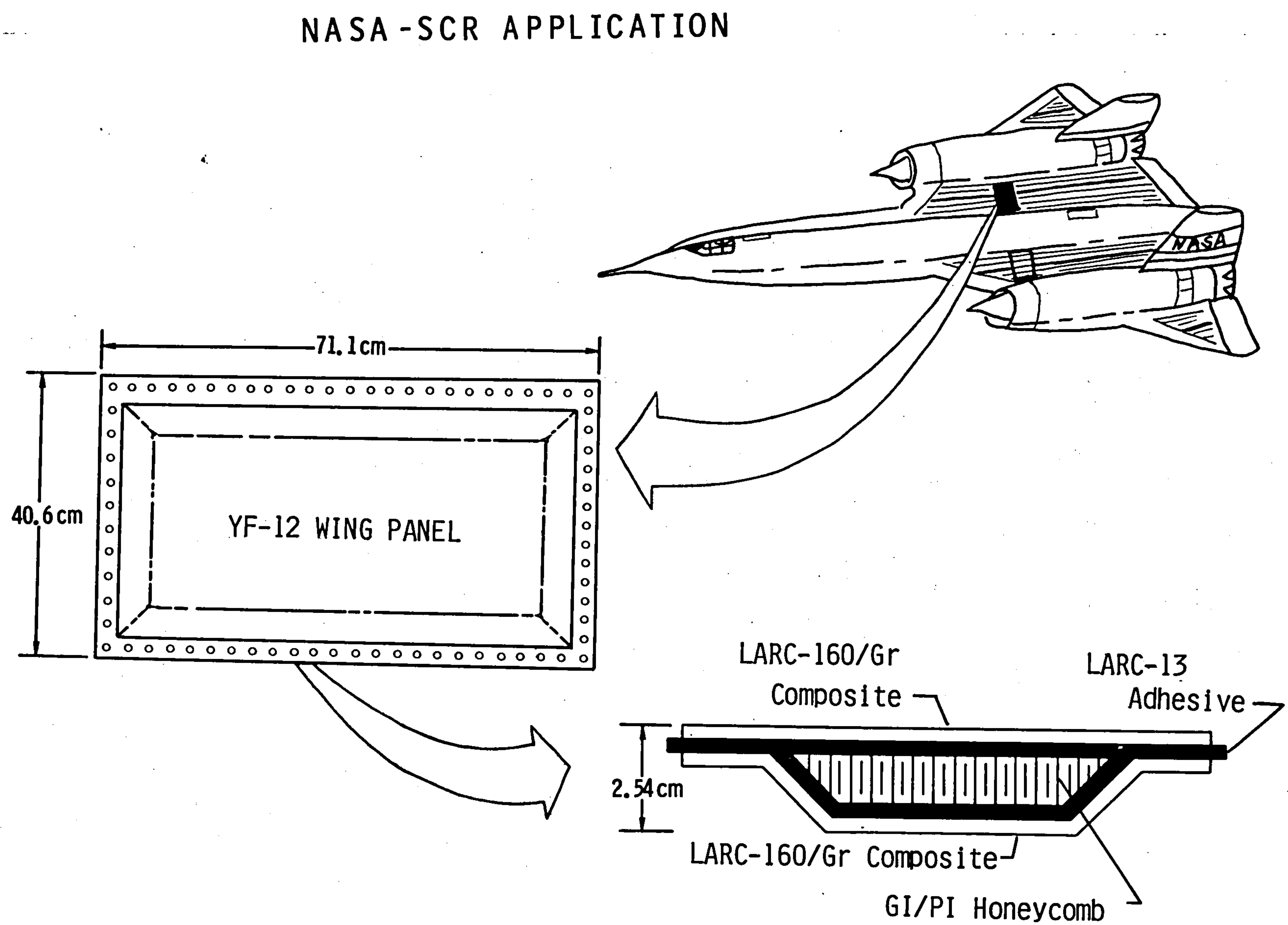

Figure 2. Polyimide composites and adhesives demonstrate high-temperature and weight-savings capabilities for aerospace applications.

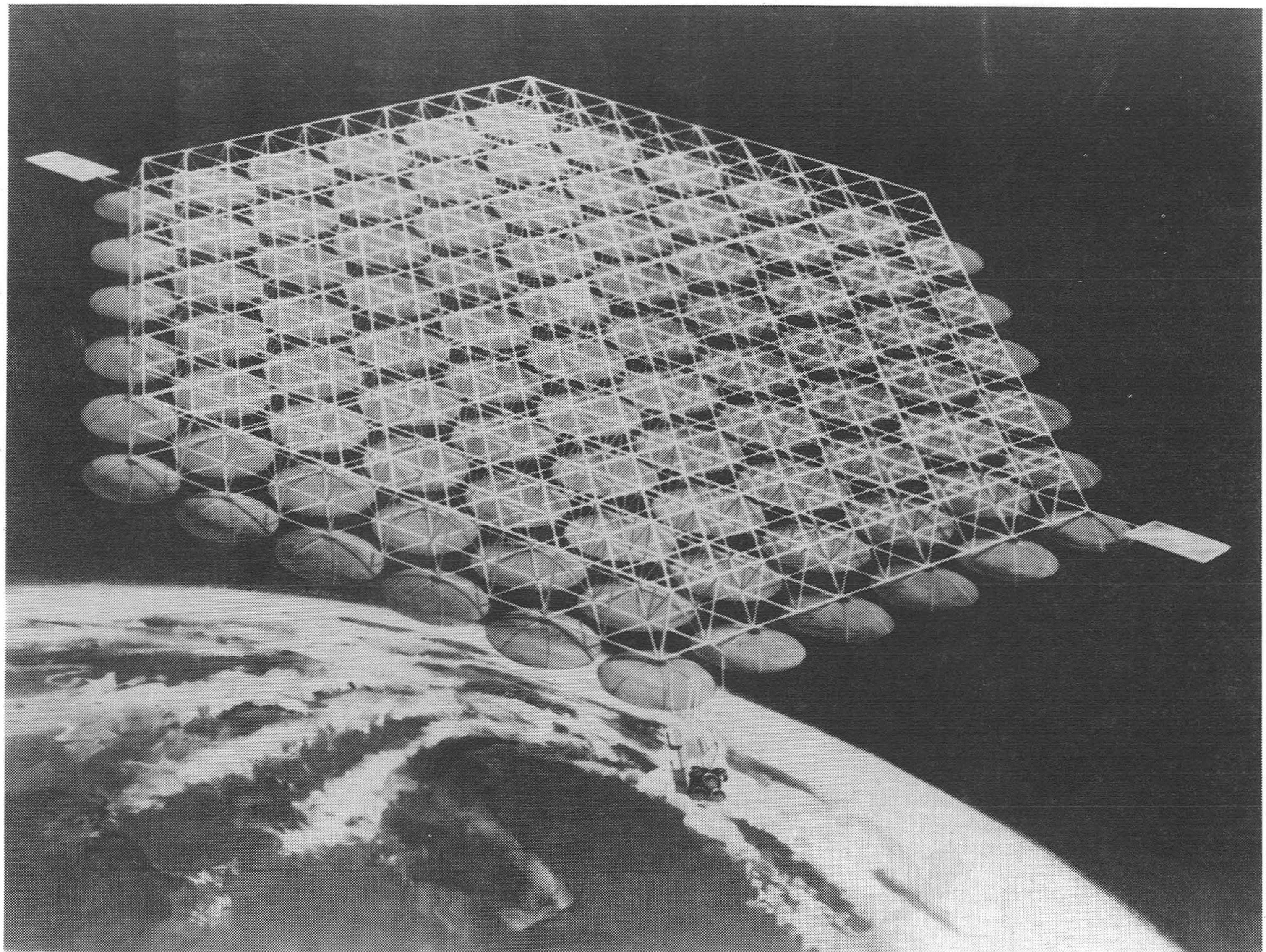

Figure 3. Large space structure of a communications antenna farm.

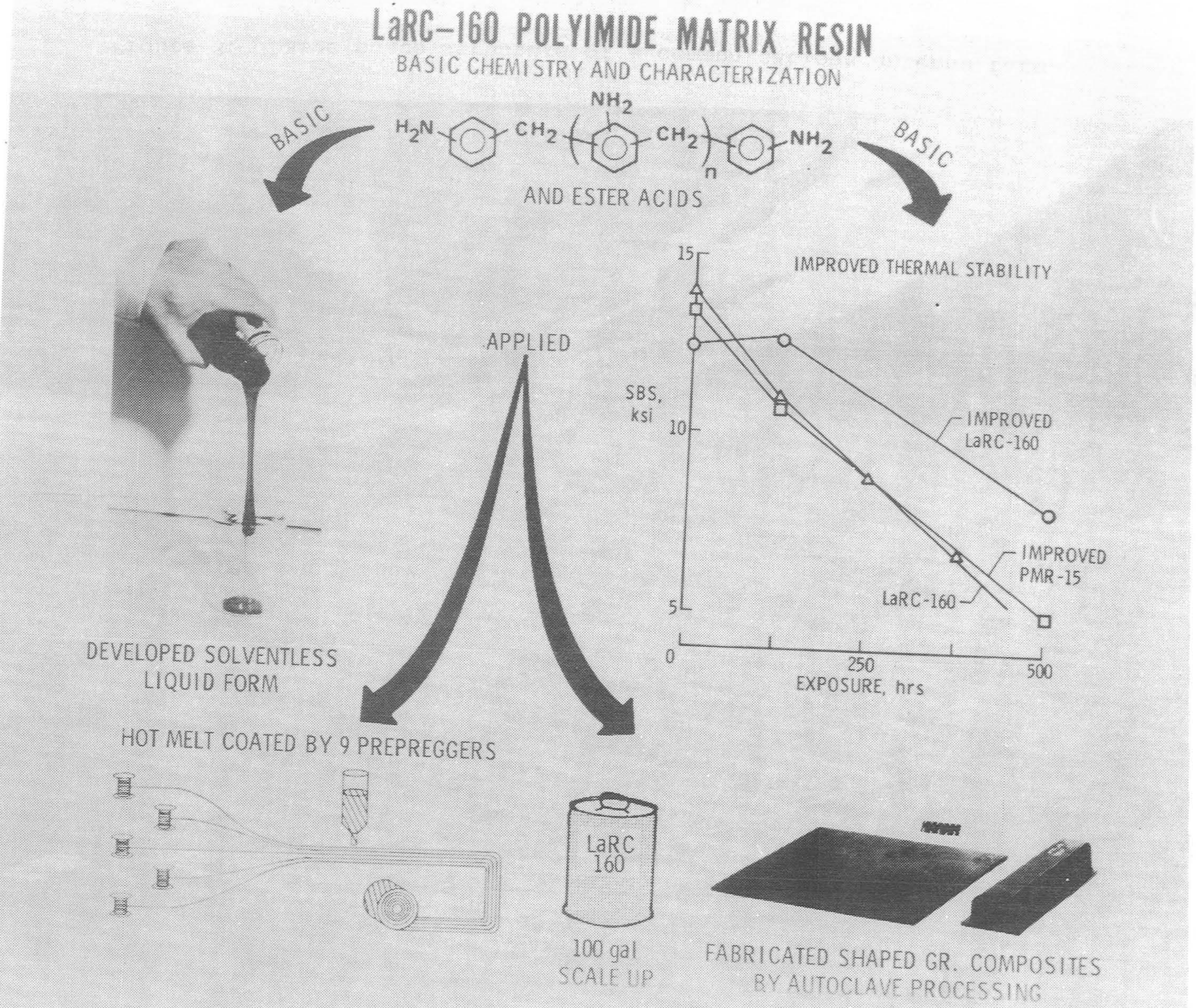

Figure 4. Solventless polyimide matrix resin approaches epoxy in processability.

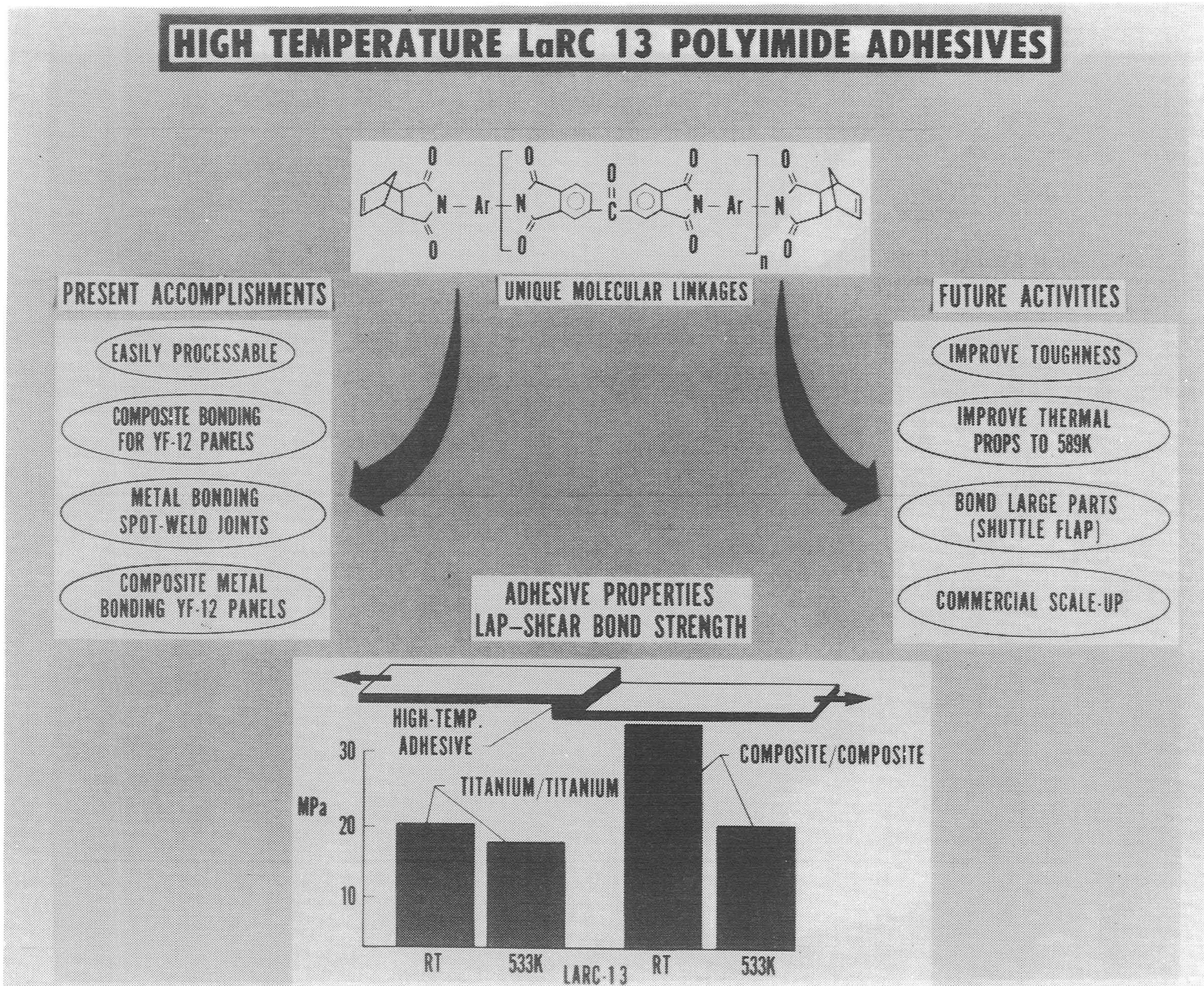

Figure 5. Polyimide adhesives show capability for bonding metals and composites.

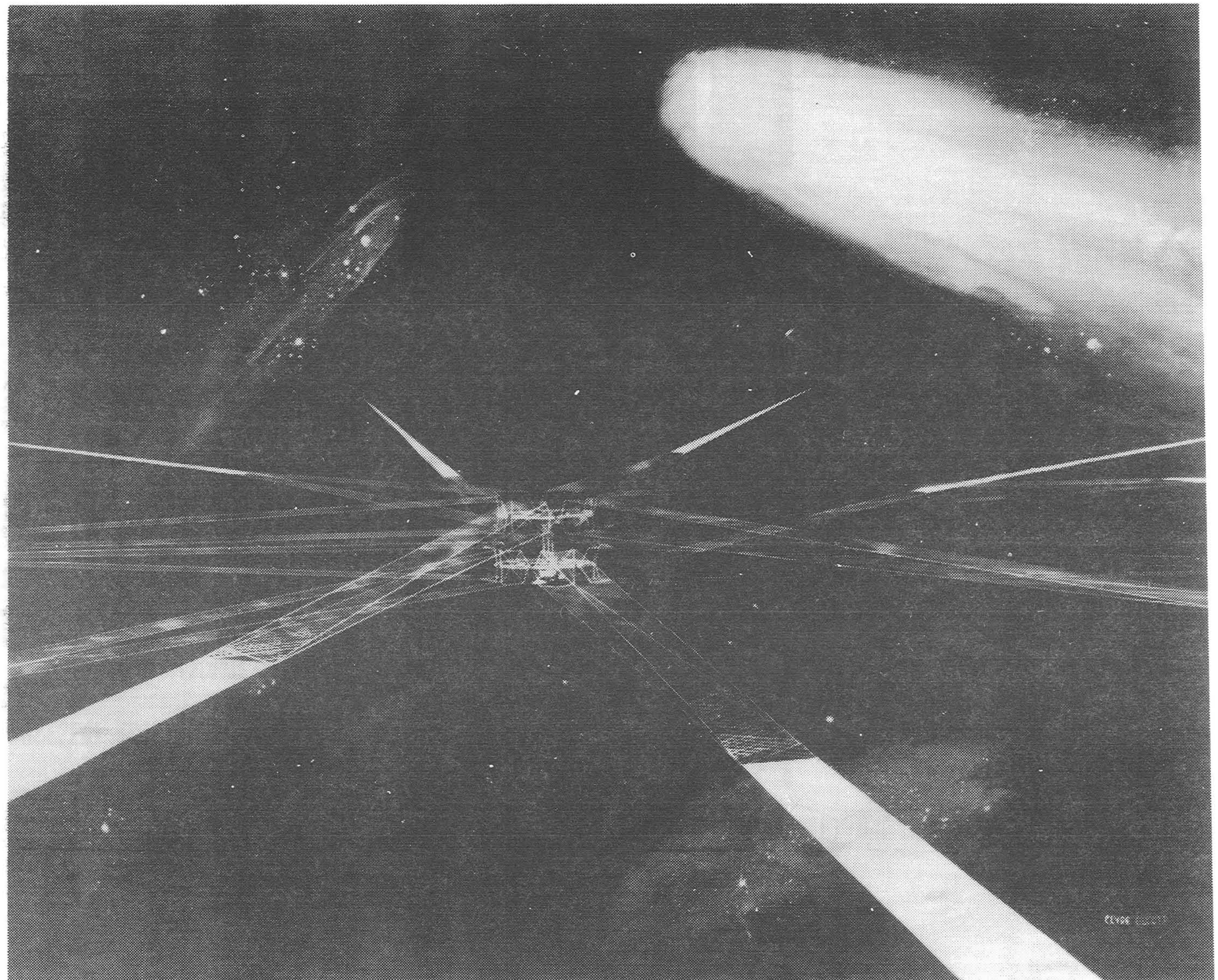

Figure 6. The heliogyro NASA-Solar Sail

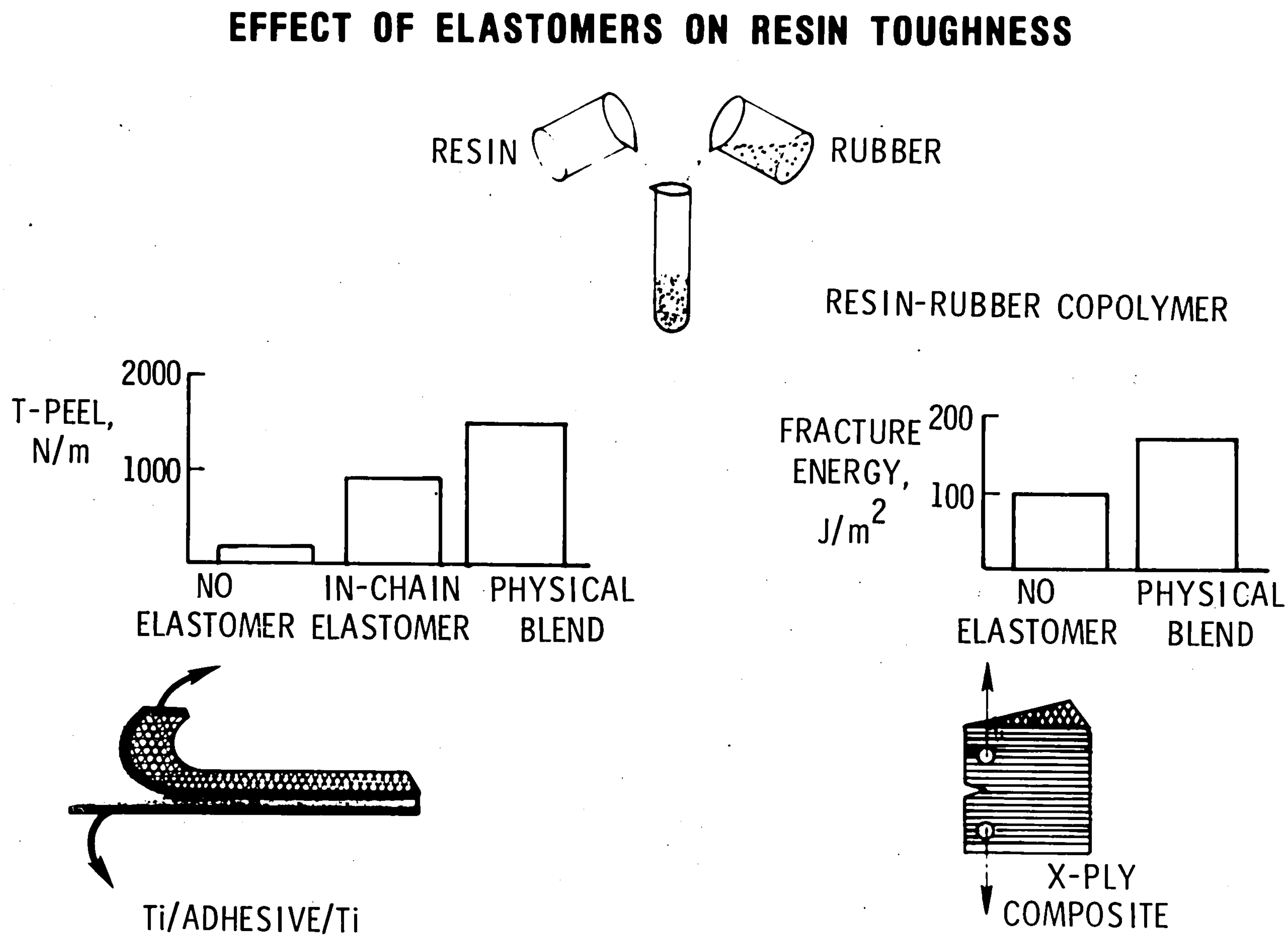

Figure 7. Elastomer-toughened polyimides show promise in the early stages of development.

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16. Abstract
This article is an up-to-date review of available commercial and experimental high-temperature polyimide resins which show potential for aerospace applications. Current government research trends involving the use of polyimides as matrix resins for structural composites are discussed. Both the development of polyimides as adhesives for bonding metals and composites, and as films and coatings for use in an aerospace environment are reviewed. In addition, future trends for polyimides are proposed.

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