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THE DEVELOPMENT OF AEROSPACE POLYIMIDE ADHESIVES

Anne K. St. Clair and Terry L. St. Clair

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Langley Research Center
Hampton, Virginia 23665

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A. K. St. Clair and T. L. St. Clair

Materials Division
NASA-Langley Research Center
Hampton, Virginia 23665

Few materials are available which can be used as aerospace adhesives at temperatures in the range of 300°C. The Materials Division at NASA-Langley Research Center has developed several novel high-temperature polyimide adhesives to fulfill the stringent needs of current aerospace programs. These adhesives are the result of a decade of basic research studies on the structure-property relationships of both linear and addition aromatic polyimides. The development of both in-house and commercially available polyimides will be reviewed with regards to their potential for use as aerospace adhesives.

INTRODUCTION

The U.S. Government and aerospace industries have escalated materials research over the past fifteen years in order to achieve ever higher levels of thermal and structural performance. However, the development of appropriate adhesives is lagging behind the production of structural aerospace materials. In an attempt to correct this situation, the government/aerospace community has begun to recognize specific adhesive needs generated by programs requiring advanced structural materials for elevated temperature applications on aircraft and spacecraft. The service life for such materials can be expected to range from the single flight of a missile lasting only a few minutes at temperatures approaching 500°C to the supersonic transport which will probably be used for at least 50,000 hours at 177°-232°C (Figure 1).

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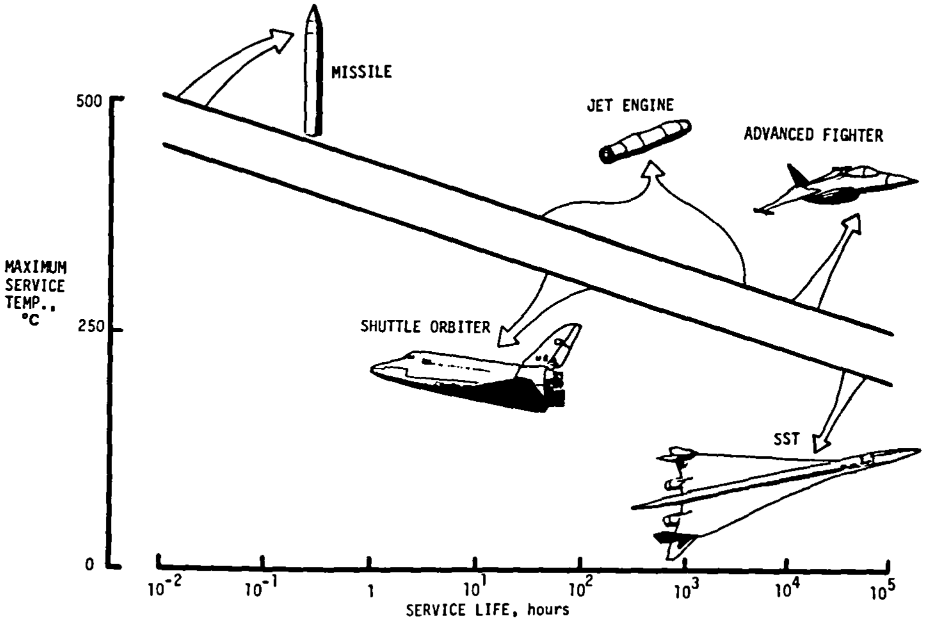

Figure 1. Time and temperature needs of advanced materials.

During the past decade, the need for high-temperature adhesives has been addressed by the National Aeronautics and Space Administration (NASA)-Langley Research Center in the Composites for Advanced Space Transportation Systems (CASTS), Supersonic Cruise Research (SCR), and the Solar Sail programs. CASTS is directed toward the development of technology to reduce the structural weight of vehicles such as the Space Shuttle through the use of high-temperature composite materials. The SCR program is designed to select and develop materials for structural applications on future supersonic transports. The Solar Sail is an outgrowth of the concept of solar wind propulsion of components in interplanetary space requiring the long-term service of materials at temperatures as high as 300°C.

At present, commercially available adhesives do not meet all of the requirements for these programs. The Materials Division at NASA-Langley is therefore conducting research to develop high-temperature adhesives for joining metals, fiber-reinforced/polymer-matrix composites and films. The materials under investigation include both linear-condensation and addition-type aromatic polyimides. This paper will review the development of both NASA in-house and commercial high-temperature polyimides. Discussions will include synthetic methods for the preparation of both linear and addition polyimides and their applicability as aerospace adhesives.

LINEAR POLYIMIDE ADHESIVES

Linear aromatic condensation polyimides are attractive candidates for aerospace adhesives because of their toughness and flexibility, remarkable thermal and thermooxidative stability, radiation and solvent resistance, low density, and excellent mechanical and electrical properties. The processing of these materials, however, is tedious compared to other engineering plastics. Traditionally, linear polyimides have been processed in the polyamic acid form because, once converted to the polyimide, they become intractable. The usual preparation of a linear aromatic polyimide (Figure 2) involves the reaction of an aromatic dianhydride with an aromatic diamine (A) in a high-boiling solvent to produce a high molecular weight, soluble polyamic acid (B). The polyamic acid is then imidized to an insoluble and thermally stable polyimide (C) by chemical conversion at ambient temperature or by heating at a high temperature (300°C) to drive off both water of condensation and solvent. Because of the volatiles generated during the cure, the preparation of large void-free adhesive joints with such a material can become exceedingly difficult.

Solvent Studies on Linear Polyimide Adhesives

Early linear polyimide adhesives[1] were prepared as amic acids in highly polar solvents such as dimethylacetamide (DMAc) or dimethylformamide (DMF). These amide solvents are retained by the polymer during the bonding process which causes the formation of detrimental voids and promotes degradation of the adhesive through transamidization (chemical interaction between the amic acid and amide solvent). In an effort to circumvent this problem with conventional amide solvents, an investigation was begun at NASA-

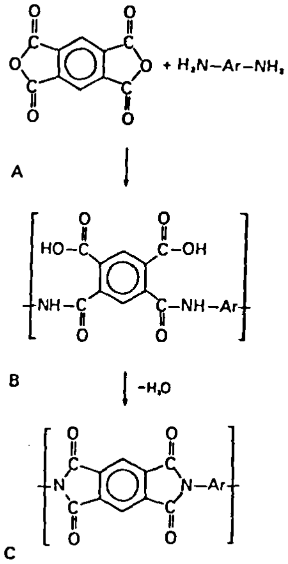

Figure 2. Method for preparing a linear aromatic polyimide.

Langley in the early 1970s to find a more suitable solvent for polyimide adhesives.

Many solvents were screened using the polymer LARC-2[2] which had been found earlier to have excellent adhesion to glass. LARC-2 (Figure 3) when prepared in DMAc or DMF is a high molecular weight polyamic acid. Polyimide films prepared by casting a 15% solids solution of this polymer onto plate glass remained flexible after a thermal cure at 300°C. However, a darkening in the yellow color of these films occurred upon curing in air which was an indication of polymer degradation. Many other solvents used in making LARC-2 also yielded high molecular weight polymer, but darkened the films during thermal imidization.

One particular series of solvents, however, did permit the polyamic acid to build to a high molecular weight and caused very little discoloration during imidization. These advantageous solvents are aliphatic ethers. Simple ethers such as diethyl ether would not properly dissolve the diamine or dianhydride monomers, but solvents such as tetrahydrofuran (THF), dioxane, and bis-(2-methoxyethyl)ether (diglyme) proved to be good solvents for both the monomers and for the resulting polyamic acid. These aliphatic ether solvents seemed to interact much less with the polyamic acid during cure than the amide solvents previously used. In addition, a remarkable increase in the adhesive lap shear strength of LARC-2 was obtained when the polymer was prepared in diglyme as shown in Table I.[3] As a result of this finding, diglyme is currently in use as a solvent for several linear polyimide adhesive systems.[4,5]

Structure-Property Relationship Studies on Linear Polyimide Adhesives

In order to observe the effect of molecular structure changes on adhesive strength, a series of linear polyimides prepared in diglyme has been screened as potential adhesives.[3,6] The effect of

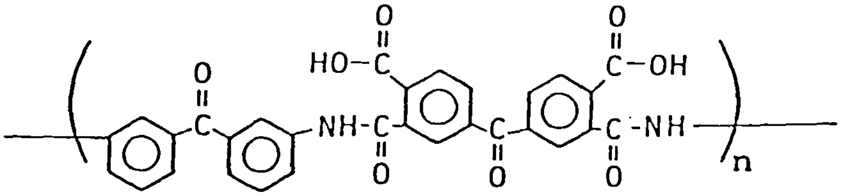

Figure 3. LARC-2 polyamic acid adhesive.

Table I. Effect of Solvent on LARC-2 Adhesive Strength.

Solvent	Lap Shear Strength, psi (MPa)*
DMF	500 (3.5)
DMAc	2500 (17)
DMAc/Dioxane	2900 (20)
Diglyme	6000 (41)

*RT test, titanium adherends

the anhydride monomer on adhesive strength is shown in Table II. In this study, an added flexibilizing group between the benzene rings of the anhydride portion of the polymer increased the adhesive lap shear strength. The effect of varying the structure of the diamine portion of the polymer is shown in Table III. A major finding in this study was the dependence of adhesive strength upon the position of attachment of the amine groups to the benzene rings. Adhesive strengths were always higher when the amine ($-NH_2$) groups were situated in the meta (3,3') position as opposed to the para (4,4') position. This amine isomer effect far outweighed any changes in flexibilizing groups between the benzene rings.

Polyimide Film Bonding Applications

During the mid 1970's, NASA had an urgent need for a flexible high-temperature adhesive that could bond ultrathin polyimide Kapton® film* as part of the proposed NASA Solar Sail program. The heliogyro sail (artist's impression shown in Figure 4) was intended for a rendezvous mission in space with Halley's Comet in 1986. An adhesive was needed to join strips of polyimide film at intervals across each of the 12 blades measuring 8 m in width by 7350 m in length. A series of linear polyimide film adhesives having both the necessary high-temperature stability and flexibility were developed for this application.[7] The series was based on LARC-2 polyamic acid (Figure 3) prepared in diglyme with the incorporation of varying amounts of pyromellitic dianhydride and the para(4,4')-

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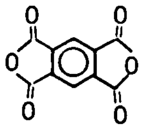
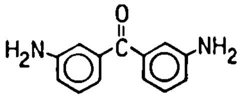
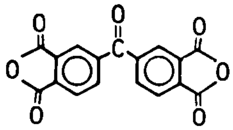
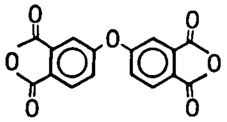
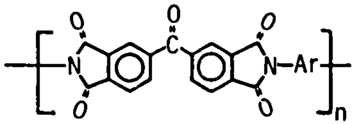
*Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

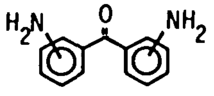
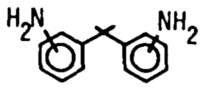
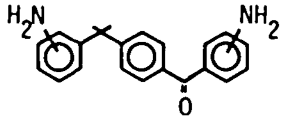
Table II. Effect of Anhydride on Polyimide Adhesive Strength.

ANHYDRIDE	AMINE	LAP SHEAR STRENGTH, psi, (MPa)*
		0 (0)
	"	6000 (41)
	"	4700 (32)

*Titanium Adherends

Table III. Effect of Diamine Isomer on Polyimide Adhesive Strength.



AMINE STRUCTURE (Ar)	AMINE ISOMER	LAP SHEAR STR., psi(MPa)*
	3,3'	6000 (41)
	3,4'	2500 (17)
	4,4'	2600 (18)
	3,3'	4200 (29)
	4,4'	1900 (13)
	3,3''	4200 (29)
	4,4''	2600 (18)

*TITANIUM ADHERENDS

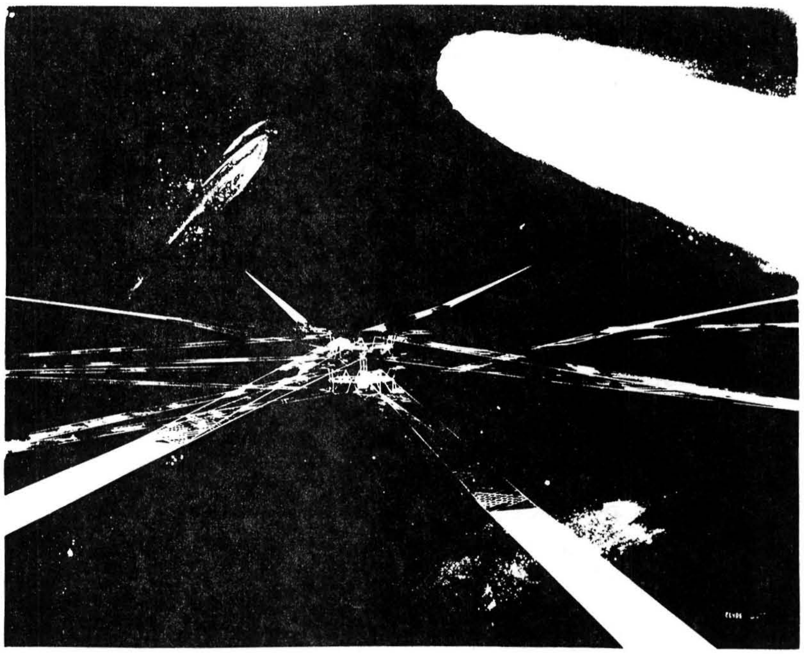


Figure 4. NASA heliogyro solar sail.

linked diamine to increase the ultimate use temperature of the adhesive. The sail joints required only a 0.64 cm overlap of film (Figure 5) which was a small enough area to allow for the escape of volatiles during the bonding process. The lap shear strengths of film specimens bonded at 316°C and aged for 6000 hrs at 275°C were 70-90 psi (480-620 kPa). This was approximately 8 times the strength required for the application. Although the LARC-2 based series of adhesives met the immediate needs of the Solar Sail program, a need still remained for an adhesive which could bond larger areas of film, metal or composites without the evolution of volatiles and entrapment of voids during cure.

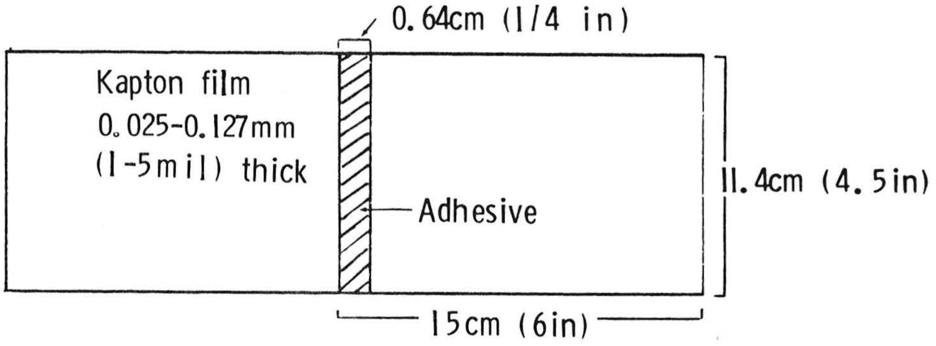


Figure 5. Schematic of bonded polyimide film specimens.

LARC-TPI Thermoplastic Polyimide Adhesive

Research on linear polyimide film adhesives progressed during the late 1970's resulting in the development of LARC-TPI in 1980. LARC-TPI[8,9] is a linear thermoplastic polyimide which can be processed in the imide form to produce large-area, void-free adhesive bonds. Like LARC-2, it is based on the BTDA and 3,3'(m,m')-DABP monomers shown in Figure 6. Unlike conventional polyimides, LARC-TPI is imidized and freed of water and solvent prior to bonding. Its thermoplastic nature is undoubtedly due to the structural flexibility introduced by bridging groups in the monomers and by the meta-linked diamine.[10] This material shows considerable potential as an adhesive because it allows the formation of large-area, voidless bonds due to thermoplastic flow.

LARC-TPI is currently being investigated as an adhesive for laminating large areas of polyimide film for both aerospace and industrial applications in the production of flexible electrical circuitry. A process[8] was recently developed at NASA-Langley for laminating polyimide films to each other or to conductive metal foils using LARC-TPI as an adhesive (Figure 7). Multi-ply laminates including metal foils may also be prepared all in one step. Kapton film laminates prepared by this method do not fail in the adhesive

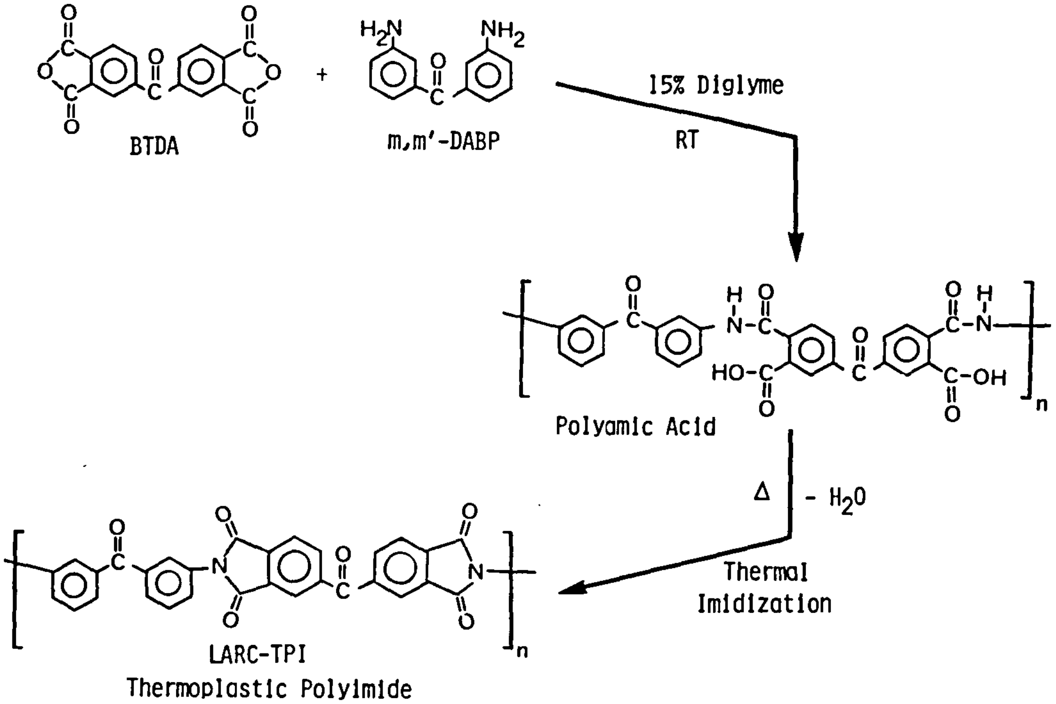


Figure 6. Preparation of LARC-TPI polyimide adhesive.

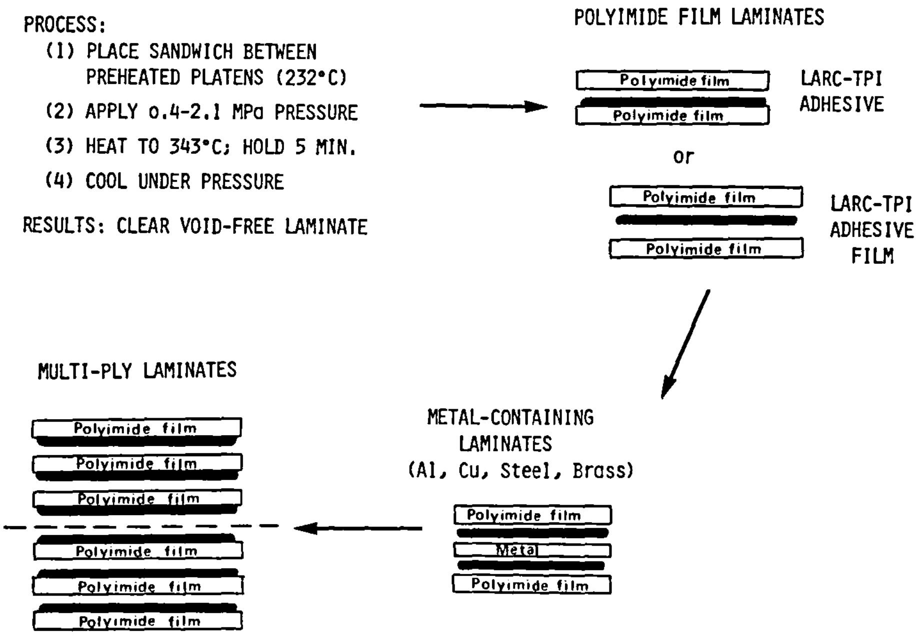


Figure 7. Process for preparing polyimide film laminates.

when subjected to standard peel tests; failure occurs through tearing of the Kapton film. Circuits (Kapton/copper/Kapton) laminated with LARC-TPI have been evaluated at the Rogers Corporation, Rogers, CT and found to withstand a ten-second immersion in a molten solder bath without blistering or delaminating.[11]

Simultaneously, LARC-TPI is being evaluated for the large-area bonding of an experimental graphite composite wing panel as part of the NASA SCR program. Preliminary bonding results on the adhesive have been generated both in-house at NASA-Langley and in studies at Boeing Aerospace Company[12] (Figure 8).

This ability to form large-area, void-free bondlines is unique for fully aromatic linear polyimide adhesives, and it makes LARC-TPI a leading candidate for future structural bonding in NASA programs. LARC-TPI is presently in the early stages of commercialization and may soon be marketed through a licensing agreement with NASA.

Linear Polyimide Adhesives Containing Metal Ions

Concurrent with the development of film adhesives was an investigation to study the effects of adding metal ions to a linear polyimide matrix.[13] Previously, the upper use temperature of linear polyimide adhesives prepared in diglyme had been extended by the addition of 30-70% by weight of aluminum powder prior to

DATA FROM	Ti/Ti LAP SHEAR STRENGTH, MPa (psi)		Ti/Ti LAP SHEAR STRENGTH AFTER 3000 hrs at 232°C MPa (psi)
	RT	232°C	232°C
BOEING AEROSPACE	36.5 (5300)	13.1 (1900)	20.7 (3000)
NASA-LANGLEY	41.4 (6000)	17.9 (2600)	—

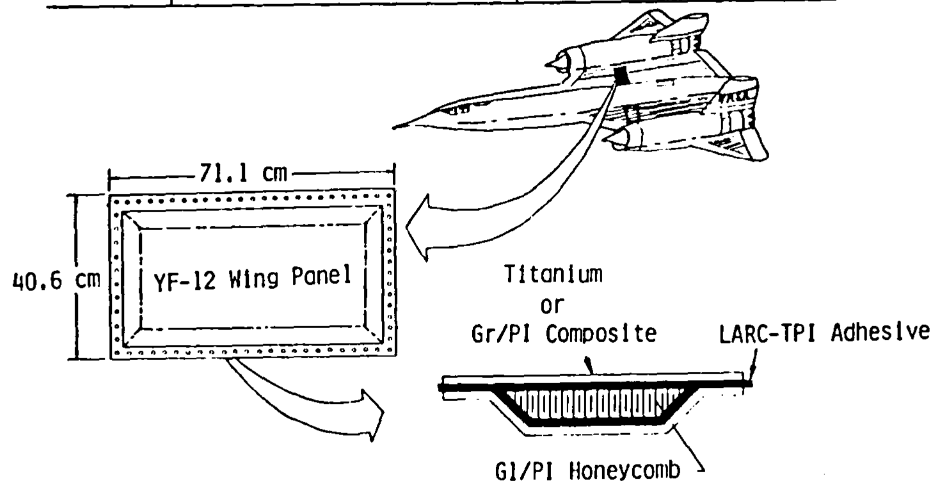


Figure 8. Structural adhesive application of LARC-TPI.

bonding.[3,6] The use of heavy metal fillers causes a large increase in bond weight and a loss in flexibility of the adhesive joint. It was discovered in the late 1970's that the high-temperature strength of a polyimide adhesive can be greatly improved by adding a small amount of aluminum ions (2% by weight) without embrittling the adhesive.[14] The structure of this metal ion-containing polymer is represented in Figure 9. Al ions are incorporated into the polyamic acid solution in the form of tri(acetylacetonato) aluminum, $Al(acac)_3$. As shown in Table IV, the addition of this organometallic complex raises the glass transition temperature (T_g) of the adhesive 20°C thus increasing its upper use temperature. This adhesive shows much promise for bonding high-temperature film for applications in space where flexibility of the bondline is a necessity.

Experimental Linear Polyimide Adhesives

A novel linear aromatic polyimide (Figure 10) having both the characteristics of linear polyphenylene oxides and sulfides has been synthesized and characterized.[15] Having a T_g of 161°C, this polyimide prepared from the flexible BDSDA and APB monomers is easily processed as a hot-melt thermoplastic. In the latter part of 1982, this material is still in the preliminary experimental stages of development as an adhesive. Room-temperature lap shear

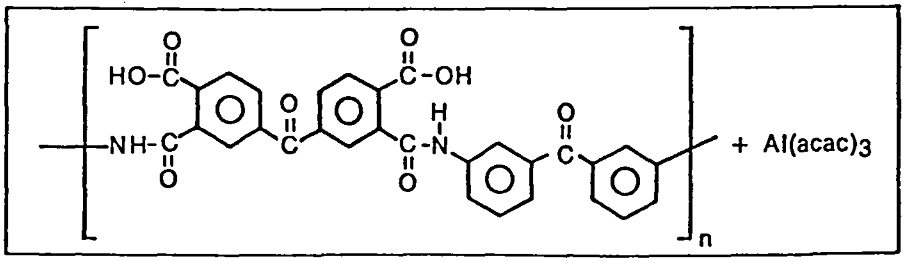


Figure 9. Aluminum ion-containing polyamic acid.

Table IV. Adhesive Strength of Al Ion-Containing Polyimide

Polyimide Adhesive	T_g, °C	Lap Shear Strength,* psi (MPa)			
		RT	250°C	275°C	300°C
Polymer Alone	251	3000 (20.7)	1600 (11.0)	0	0
With $Al(acac)_3$	271	2400 (16.5)	1900 (13.1)	1600 (11.0)	700 (4.8)

*Titanium adherends

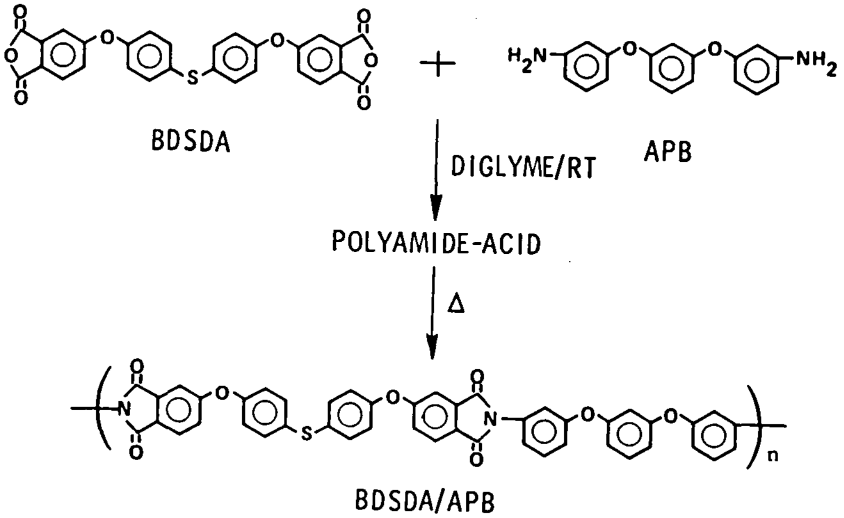


Figure 10. Polymer synthesis of a hot-melt adhesive.

strengths for this adhesive bonded to titanium adherends are averaging 6,000 psi (42 MPa) which is unusually high compared to strengths of conventional polyimide adhesives. Although its upper use temperature is somewhat limited by its T_g, this polyethersulfideimide shows excellent potential as a highly processable hotmelt adhesive.

An experimental polyimidesulfone[16] is also under current investigation at NASA-Langley for use as an engineering thermoplastic. This novel polymer system (Figure 11) has the advantageous thermoplastic properties generally associated with polysulfones, and the added solvent resistance and thermal stability of aromatic polyimides. Because of its improved processability over the base polyimide, the polyimidesulfone can be processed in the range of 260°-325°C to yield strong, high-temperature resistant adhesive bonds. Initial studies indicate high lap shear strengths of 4500 psi (31.0 MPa) for polyimidesulfone adhesive bonds prepared using titanium adherends, and good retention of strength (2600 psi, 17.9 MPa) at 232°C. The combination of properties offered by this material make it attractive for structural adhesives applications for aircraft and spacecraft.

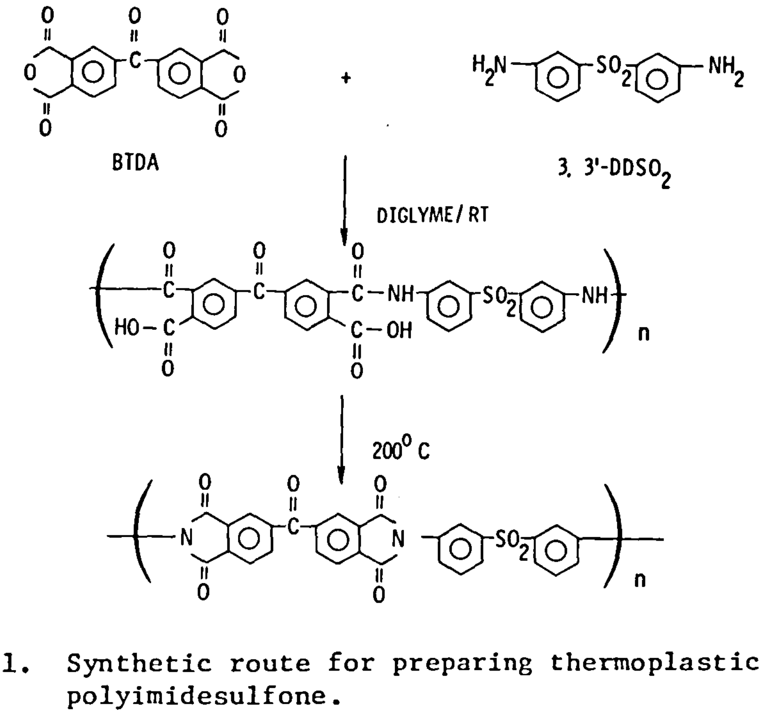


Figure 11. Synthetic route for preparing thermoplastic polyimidesulfone.

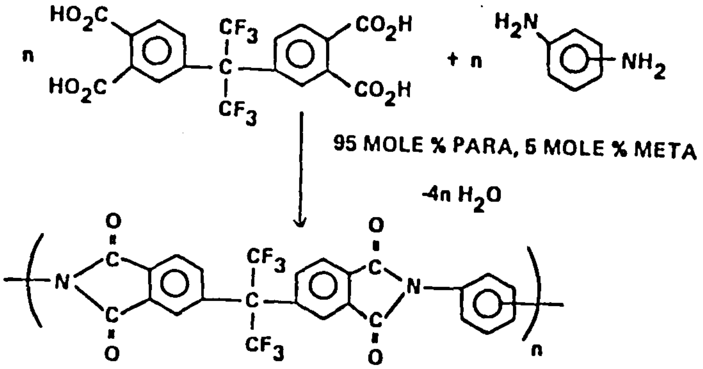


Figure 12. Preparation of DuPont's NR-150B2.

Commercial Linear Polyimide Adhesives

Linear polyimides have rarely been commercially available for use as adhesives. In 1972, DuPont began marketing a series of linear aromatic polyimides called NR-150.[17] This series was based on the highly thermooxidatively stable monomer 2,2-bis(3',4'-dicarboxyphenyl)hexafluoropropane (6F). NR-150B2 shown in Figure 12 displayed excellent high-temperature adhesive properties, but was difficult to process because of the presence of condensation volatiles and a high-boiling solvent. In spite of these processing difficulties, this material was widely evaluated as a structural adhesive until its removal from the market in 1980.

Several other linear aromatic polyimide adhesives have been available over the past decade from companies such as Monsanto (Skybond series), American Cyanamid (FM-34), Amicon, Hexcel and U.S. Polymeric. However, the chemical structures of the polyimide products from these companies have been withheld as proprietary. Due to a general lack of information, these polyimide products will not be discussed here in any detail. Of the products mentioned, American Cyanamid's FM-34 has probably been the most widely used as an adhesive. This adhesive was recently evaluated in the NASA CASTS program for bonding titanium and graphite/polyimide composites.[18] It is capable of bonding small areas for applications at 316°C and is suited for large-area bonding if the joint is well vented to allow for ample escape of volatiles.

A new linear polyimide called Ultem was commercialized in early 1982 by the General Electric Company.[19] This new polyetherimide is reported to be unique in high-performance plastics because of its processability. Ultem exhibits good mechanical strength, flame retardance, and chemical and radiation resistance. Although this material has not been evaluated as an adhesive, it may have potential for adhesive applications where extended use temperatures will be in the range of 170°C.

As of this writing, the most recent polyimide products to become commercially available are FM-36 adhesive film and FM-30 adhesive foam introduced in late 1982 by American Cyanamid.[5] These materials are currently being promoted as aerospace adhesives, serviceable over the temperature range of -55°C to 287°C. FM-36 is a modified polyimide which is supplied as a film supported by 112 glass cloth. A follow-up to FM-34, these materials are thought to be linear polyimides although no chemical structures have been disclosed by the manufacturer.

ADDITION POLYIMIDE ADHESIVES

Attempts have been made over the past decade to alleviate the processing difficulties associated with high-temperature linear polyimides through use of addition-type polymers. Addition polymers are easily processed in the form of short-chained oligomers which thermally chain extend by an addition polymerization involving reactive unsaturated end groups. Although much has been gained toward alleviating the evolution of volatiles associated with linear systems using this method of polymerization, the addition-type polyimides which have been developed are thermosets which cure to form a highly crosslinked network. In comparison to a linear system, these crosslinked networks are very brittle.

Development of Nadic-Terminated Addition Polyimides

In the late 1960's TRW developed a route for preparing short-chained aromatic imides endcapped with 5-norbornene-2,3-dicarboxylic (nadic) anhydride (Figure 13).[20] The final cure of this polymer called P-13N was effected by the thermal chain extension of olefinic end groups on the nadimide prepolymer to produce an essentially void-free, highly crosslinked polymer.

Unfortunately, a problem exists with the nadic-capped addition polyimides which is two-fold. First, the nadic portion of this material contains aliphatic groups which somewhat reduce the long-term thermal stability of the resulting polymer. Second, nadic-capped imides must be cured under pressure in order to prevent a

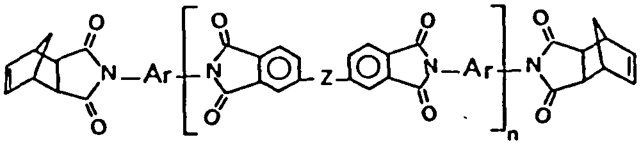


Figure 13. Nadic-terminated imide oligomer.

retrograde Diels-Alder reaction from occurring which would dissociate the molecule into two components[21] (Figure 14). One of the possible components is a volatile chemical, cyclopentadiene, which can be detrimental in preparing void-free components or adhesive bonds.

Structure-Property Relationship Studies of Nadic-Terminated Addition Polyimide Adhesives

Although the first nadic-terminated imides were more readily processable than linear polyimides, they did not perform well as adhesives. For the purpose of developing a nadic-capped system with good adhesive properties for aerospace applications, NASA-Langley began a structure-property relationship study of addition polyimides in the mid 1970's to better understand how molecular structures affect adhesive properties.[22]

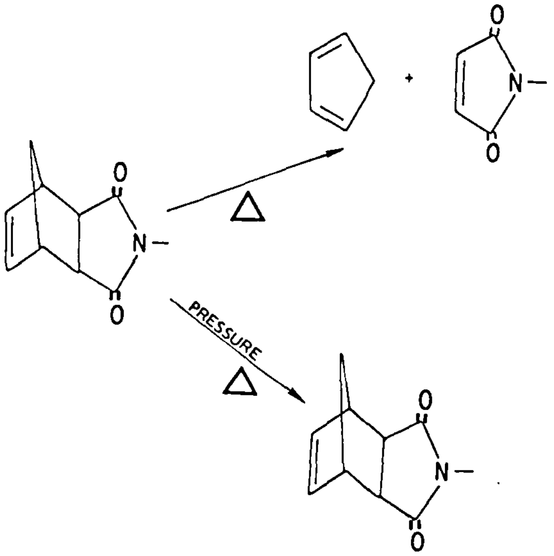
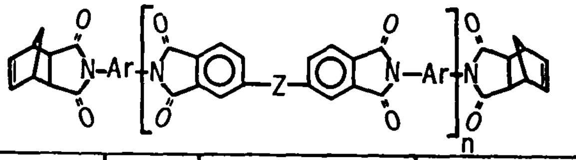
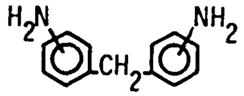
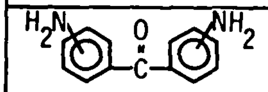


Figure 14. Reaction products from the cure of nadic-capped imides.

Table V. Adhesive Properties of Nadic-Terminated Imides.



AMINE STRUCTURE (Ar)	Z	AMINE ISOMER	LAP SHEAR STR., psi(MPa)*
	$-\underset{\overset{\|}{O}}{C}-$	3,3'	2800 (19)
	$-\underset{\overset{\|}{O}}{C}-$	4,4'	600 (4)
	-O-	3,3'	2500 (17)
	-O-	4,4'	1300 (9)
	$-\underset{\overset{\|}{O}}{C}-$	3,3'	2100 (14)
	$-\underset{\overset{\|}{O}}{C}-$	4,4'	1300 (9)
	-O-	3,3'	3000 (21)
	-O-	4,4'	1300 (9)

*TITANIUM ADHERENDS

The addition polyimides which were screened for their potential as structural adhesives for bonding titanium adherends are listed in Table V. The material which is listed second in Table V prepared from the para (4,4')-methylenedianiline was the only commercially available material at the time this study was conducted. It also had the poorest adhesive strength of any of the systems tested. As was found previously in the evaluation of linear polyimide adhesives, the addition polymers containing the meta (3,3')-linked aromatic diamines were superior adhesives. The first nadimide listed in Table V (later designated as LARC-13) exhibited the highest lap shear strength and has been further developed as a structural adhesive for specialized bonding in the NASA CASTS[18] and SCR[23] programs as well as for other aerospace applications.[24,25,26]

LARC-13 Addition Polyimide Adhesive

LARC-13 is a nadimide addition-curing adhesive which has been developed by NASA for "low pressure" bonding without the generation of volatiles during cure.[23] The synthetic route for preparing LARC-13 is displayed in Figure 15. Because it has a high degree of

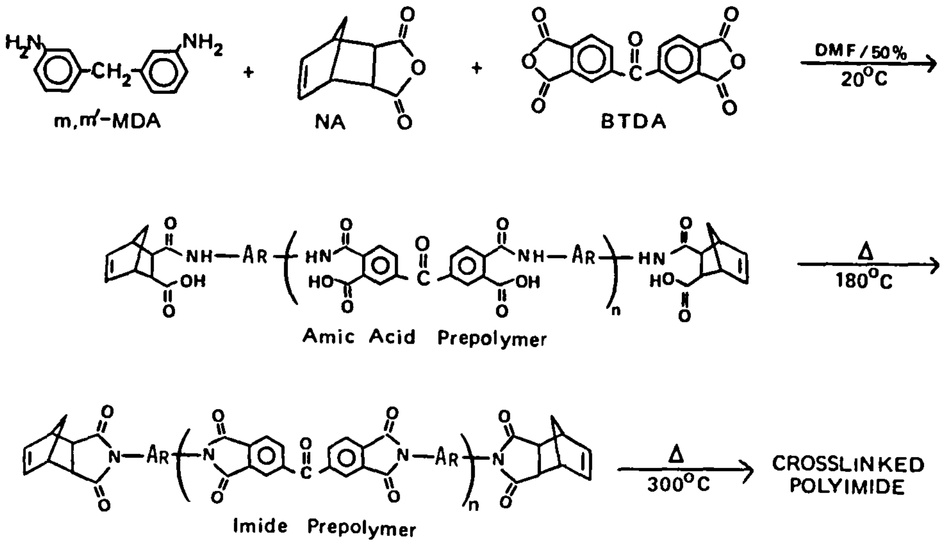


Figure 15. Synthetic route for preparing LARC-13 adhesive.

flow during cure, it is easily autoclave processable. This ease of flow is attributed to the presence of the meta-linked aromatic diamine.

Because of its high crosslink density, LARC-13 can be used well in excess of its glass transition temperature of 270°C. It has been used successfully to bond a high-temperature composite to a ceramic for missile applications requiring several seconds performance at 595°C. LARC-13 has also met criteria for NASA CASTS applications exhibiting adequate adhesive strength after 125 hrs. aging at 316°C. A major usage of this adhesive has been in the bonding of honeycomb sandwich structures where the following are required: (1) bond at low pressure of 50 psi (345 kPa) in order not to collapse the honeycomb structure and (2) fillet around the cell structure. LARC-13 has met both of these requirements. As part of the NASA SCR program, LARC-13 is being evaluated by both NASA-Langley and Boeing Aerospace Company for bonding titanium and polyimide/graphite composites. Bonding data from both centers are shown in Table VI.

Elastomer-Toughened Addition Polyimide Adhesives

In early 1979 an investigation was begun at NASA-Langley to determine the effects of incorporating elastomers into the brittle

Table VI. LARC-13 Lap Shear Strengths.

Laboratory	Adherend	Lap Shear Str., psi (MPA)	
		RT	316°C
NASA-Langley	Gr/PMR-15	2300 (16)	1900 (13)
	Gr/NR-150B2	5000 (35)	1700 (12)
	Titanium	3000 (21)	1500 (10)
Boeing	Gr/PMR-15	2000 (14)	2000 (14)
	Glass/PMR-15	3300 (23)	2200 (15)
	Titanium	4000 (28)	2200 (15)

LARC-13 adhesive matrix. Butadiene/acrylonitrile and silicone elastomers were incorporated into the polyimide resin to study the effects on polymer glass transition temperature (Tg), thermal stability, adhesive strength, and fracture toughness.[27] Two approaches were used to add elastomers to LARC-13 (Figure 16). Fluorosilicone (Silastic) and vinyl-terminated silicone (Sylgard) elastomers were physically blended into the LARC-13 amic acid

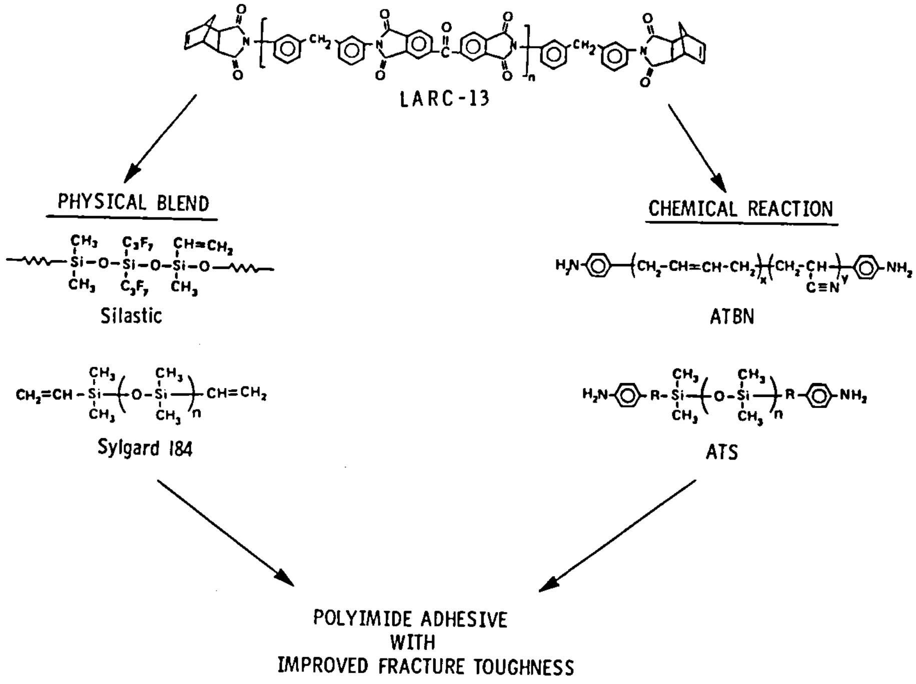


Figure 16. Preparation of elastomer-modified LARC-13 addition polyimides.

Table VII. Lap Shear Strengths (LSS) of Elastomer-Toughened LARC-13/Titanium Bonds.

Adhesive	LSS, psi (MPa) Samples Unaged			LSS, psi (MPa) Aged 500 hrs @ 232°C		
	RT	232°C	288°C	RT	232°C	288°C
LARC-13	2900 (20)	2800 (19)	1300 (9)	2900 (20)	2900 (20)	2200 (15)
LARC-13/ Silastic	2200 (15)	1800 (12)	500 (3)	1600 (11)	1800 (12)	1300 (9)
LARC-13/ Sylgard	3300 (23)	2400 (17)	-	2500 (17)	2300 (16)	-
LARC-13/ ATBN	3700 (25)	2800 (19)	-	2000 (14)	1900 (13)	-
LARC-13/ ATS	2600 (18)	1800 (12)	900 (6)	1700 (12)	1600 (11)	1400 (10)

adhesive; and aromatic amine-terminated butadiene/acrylonitrile (ATBN) and silicone (ATS) elastomers were chemically reacted into the prepolymer backbone.

Each of the four modified resins displayed a separate phase for the elastomer and LARC-13 moieties as indicated by a T_g at low temperature (-115° to -65°C) and at high temperature (277° to 300°C). Incorporation of elastomer particles at a concentration of 15% solids by weight resulted in a six- to seven-fold increase in peel strength and a three- to five-fold increase in the fracture toughness of LARC-13. This improvement in toughness was accomplished at a sacrifice in the elevated temperature adhesive strengths of the elastomer-modified materials as shown in Table VII. It was noted, however, that the 288°C strengths of the elastomer-modified LARC-13 bonds improved after aging at elevated temperature. This behavior is probably due to latent crosslinking of the elastomer with the polyimide.

An additional study was conducted in mid 1980 to observe the effect of the elastomer chain length on the properties of LARC-13 addition polyimide adhesive.[28] A new series of polymers was synthesized using amine-terminated silicones of varying chain lengths. Four ATS elastomers (Figure 16) prepared with chain lengths varying

Table VIII. Lap Shear Strengths of LARC-13 Modified With ATS Elastomers of Varying Chain Lengths.

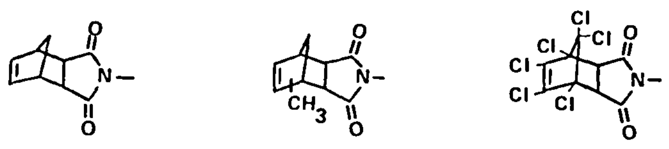
Adhesive	LSS, psi (MPa) Unaged Samples			LSS, psi (MPa)* Aged 500 hrs @ 232°C		
	RT	232°C	288°C	RT	232°C	288°C
LARC-13	2900 (20)	2800 (19)	1300 (9)	2900 (20)	2900 (20)	2200 (15)
LARC-13/ ATS_{105}	2600 (18)	1800 (12)	900 (6)	1700 (12)	1600 (11)	1400 (10)
LARC-13/ ATS_{63}	2600 (18)	1400 (10)	700 (5)	1600 (11)	1600 (11)	1300 (9)
LARC-13/ ATS_{41}	2500 (17)	1800 (12)	800 (6)	1700 (12)	1600 (11)	1400 (10)
LARC-13/ ATS_{10}	2900 (20)	1800 (12)	700 (5)	1800 (12)	1700 (12)	1400 (10)
LARC-13/ $ATS_{105} + ATS_{10}$	3000 (21)	2100 (14)	1300 (9)	2300 (16)	1900 (13)	1700 (12)

* Titanium Adherends

from $n = 10$ to $n = 105$ were reacted into the LARC-13 backbone at a concentration of 15% solids by weight. An additional LARC-13/ATS formulation was prepared for this study using a 50:50 combination of ATS elastomers having repeat units of 105 and 10. The adhesive lap shear strengths of these five resins are compared to that of LARC-13 in Table VIII. Results from the lap shear tests showed that variation of the elastomer chain length had very little effect on the adhesive properties of ATS-modified LARC-13. An important finding, however, was the significant increase in strength displayed by the LARC-13 formulation containing a 50:50 bimodal distribution of elastomers ATS_{105} and ATS_{10}. This adhesive containing elastomers of both long and short chain lengths shows potential as an aerospace adhesive for selected high-temperature applications.

Variation of End Caps on Addition Polyimide Adhesives

Although nadic-terminated imides offer considerable processing advantages, they cannot withstand long-term elevated temperatures in air without gradually degrading. An investigation was conducted to find a crosslinking end group which would improve the thermo-oxidative stability of LARC-13 adhesive. A second objective was to find a latent crosslinking end cap which would allow a cure without the evolution of cyclopentadiene (Figure 14). The end groups evaluated in this study are shown in Figure 17. Six novel addition polyimides were synthesized using these end caps and were characterized for solubility, melt-flow and cure properties, T_g, thermal stability and adhesive strength.[29] Of the polymers tested, only the hexachloro-nadic and nadic-capped LARC-13 outgassed a cyclopentadiene on curing. The LARC-13 nadic, acetylene, and N-propargyl-containing polymers exhibited excellent adhesive bond strengths on titanium at both ambient and elevated temperature compared to the other four polymers. As shown in Table IX, the acetylene-capped addition polyimide had 40% greater stability (adhesive strength) than nadic-capped LARC-13 after aging 1000 hrs at elevated temperature.



NADIC CH$_3$-NADIC Cl$_6$-NADIC

N-PROPARGYL ACETYLENE

CYCLOHEXENE MALEIC

Figure 17. Crosslinking end groups for LARC-13 adhesive.

Table IX. Lap Shear Strengths of Titanium/ Addition Polyimide Bonds Aged for 1000 Hours at 232°C

Oligomer End Group	LSS, psi (MPa) Unaged Sample		LSS, psi (MPa) after 1000 hrs @ 232°C	
	RT	232°C	RT	232°C
Nadic	3200 (22)	2600 (18)	2600 (18)	2000 (14)
Acetylene	2900 (20)	2500 (17)	2500 (17)	2800 (19)
N-Propargyl	3100 (21)	2800 (19)	800 (6)	1000 (7)

Commercial Addition Polyimide Adhesives

Of the few aromatic addition polyimide adhesives that have been available commercially, Thermid 600 is the most attractive for use at elevated temperature and therefore shows the most potential as an aerospace adhesive. In 1969, Hughes Aircraft Company prepared a series of novel acetylene-terminated imide oligomers which could be thermally polymerized through the ethynyl end group. Initiated under the sponsorship of the U.S. Air Force Materials Laboratory (AFML)[30] the work was not made public until 1974.[31,32] The oligomer shown in Figure 18 was designated HR600 by Hughes and is presently marketed by Hughes Aircraft Company under the tradename of Thermid 600.[33] Thermid MC-600 is the fully imidized molding powder; and Thermid LR-600 is the amic acid form of the oligomer in N-methylpyrrolidone. Both show promise as high-temperature structural adhesives and have been effective in bonding titanium, aluminum, copper, and composites. The LR-600 has been most widely evaluated as an adhesive resin. Though it exhibits excellent thermomechanical properties at temperatures approaching 316°C, it has an inherent drawback in that its gel time is very short on the order of 100-180 seconds. This short gel time (flow life) is the cause of reduced adhesive lap shear strengths at both ambient and elevated temperatures. Work has been done to improve upon this system at the University of Dayton Research Institute and AFML.[34] Researchers have found that the addition of various cure inhibitors greatly increase the gel time of Thermid 600 while improving flow and titanium alloy wetting. Room temperature lap shear strengths of 3800 psi (26 MPa) have been obtained on titanium adherends by

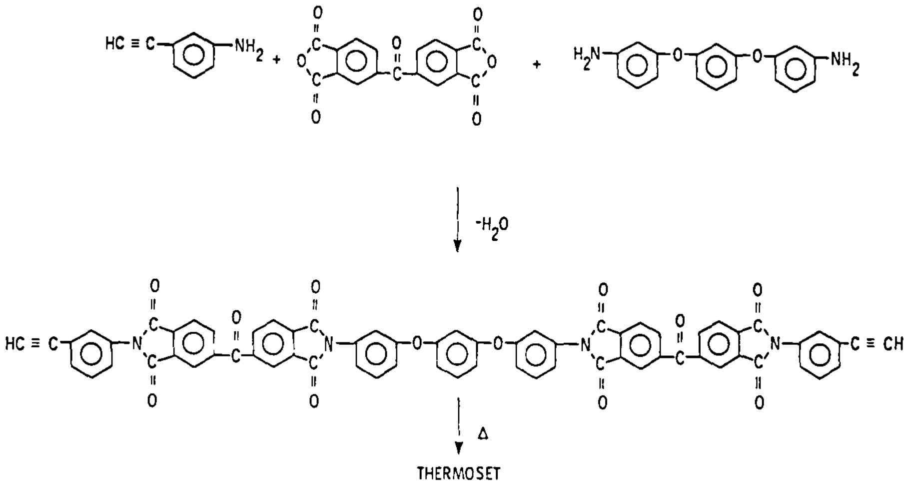


Figure 18. Thermid 600 resin chemistry.

the addition of 5% hydroquinone to the LR-600 resin. The addition of hydroquinone also enhances the high-temperature (316°C) strength of this adhesive (1650 psi, 11.4 MPa), but at the same time somewhat reduces the long-term thermooxidative stability of the polymer. Current studies at Hughes involve the examination of modified HR600 resins geared at improving heat resistance and resistance to fatigue.[35]

Another class of addition-type polyimides which have been offered commercially are the bismaleimides. In 1973, the development of maleimide-capped oligomers was reported by Rhone-Poulenc.[36] These materials were then marketed in the U.S. by Rhodia as a product line called Kerimid. Although bismaleimides are being used for a variety of applications, they have not shown strong potential as high-temperature adhesives due to their limited thermal stability.

SUMMARY

High-temperature adhesives are becoming increasingly important for aerospace applications. At the present time there are very few high-temperature adhesives available commercially, and none of these are able to satisfy all of the stringent needs of current aerospace programs. The Materials Division at NASA-Langley Research Center is screening both commercial and in-house experimental aromatic polyimides for use as structural adhesives on NASA-funded programs. The polyimide adhesives being developed at NASA-Langley are the result of basic research studies conducted over the last decade on the structure-property relationships of both linear and addition polyimides.

Solvent and structure studies on linear aromatic polyimides have progressed to the development of LARC-TPI, a fully imidized thermoplastic polyimide which can be processed as an adhesive in the imide form to yield void-free bondlines. LARC-TPI shows much promise as a structural adhesive for bonding metals and composites and as an adhesive for laminating film for flexible electronic circuitry. Additional studies have shown that the upper use temperature of linear polyimide adhesives can be extended by the addition of small amounts of Al(III) ions.

Structure-property studies on addition polyimides have led to the development of LARC-13, a nadic-capped imide oligomer which is currently being used to bond both titanium and composites for several aerospace applications. Research on LARC-13 has shown that this type adhesive is more readily processable than a linear system, but less thermooxidatively stable and more brittle. However, because of its high crosslink density, the addition adhesive is able to perform at least for short terms at elevated temperatures up to 600°C where linear systems fail thermoplastically.

Active research goals on both linear and addition aromatic polyimide adhesives geared to meet future needs include: (1) Improved processability of thermoplastic polyimides for use as hot-melt adhesives; (2) Use of a polyimidesulfone adhesive to obtain both improved processability and solvent resistance; (3) Improved fracture toughness of addition polyimide adhesives by incorporating heat-resistant elastomers; and (4) Improved thermooxidative stability of addition polyimide adhesives through chemical modifications.

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16. Abstract

Few materials are available which can be used as aerospace adhesives at temperatures in the range of 300°C. The Materials Division at NASA Langley Research Center has developed several novel high-temperature polyimide adhesives to fulfill the stringent needs of current aerospace programs. These adhesives are the result of a decade of basic research studies on the structure-property relationships of both linear and addition aromatic polyimides. The development of both in-house and commercially available polyimides will be reviewed with regards to their potential for use as aerospace adhesives.

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