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# HIGH TEMPERATURE ADHESIVES FOR STRUCTURAL APPLICATIONS: A REVIEW

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# HIGH TEMPERATURE ADHESIVES FOR STRUCTURAL APPLICATIONS - A REVIEW

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**SUMMARY**

The requirement for high temperature adhesives in the aero engine industry is assessed and the reasons for the choice of polyimide adhesives as prime candidates are discussed. Cure chemistry of these resins is described and the recent development of polyimides that cure by addition mechanisms is reviewed. Currently available adhesives are listed and two typical formulations (FM34 and A7F) are discussed in more detail giving some "as cured" and thermally aged" properties. The necessity for the provision of special accessory materials and curing facilities in order to process these adhesives at the required temperatures is explained.

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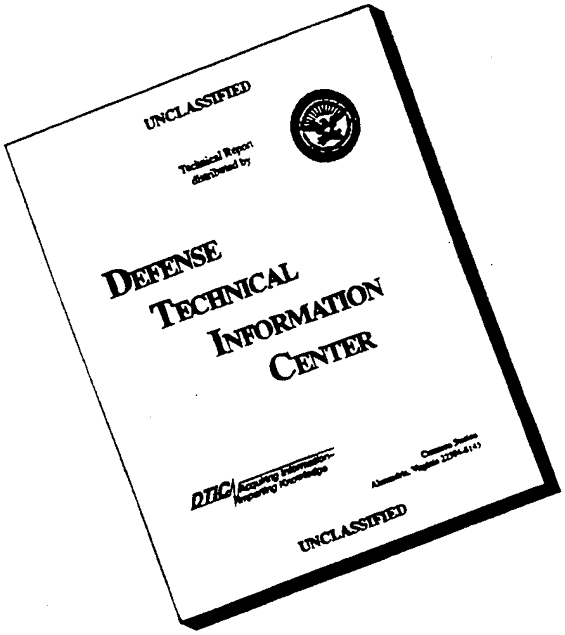


## INTRODUCTION

In recent years, considerable efforts have been made to improve the fuel consumption of commercial aircraft because of the steeply increasing cost of aviation fuels. An effective means of achieving this end is to significantly reduce the weight of the aircraft and engine installations by the replacement of metal components with fibre reinforced composite. Substitution of CFRP for aluminium can produce a 30% weight saving, and elimination of higher density metals (where possible) can produce even greater savings.

The efficient utilisation of composites requires the incorporation of adhesively bonded joints to replace mechanical fasteners, i.e. rivets, bolts etc. At Rolls-Royce Ltd., fibreglass reinforced composites bonded with structural adhesives have been used on the RB 162 and RB 211 since their inception. Today, carbon fibre reinforced composites are rapidly being introduced into the RB 211 powerplant (1) and the requirement for a wide variety of structural adhesives is increasing. Table 1 gives a list of the applications for structural epoxy adhesives at Rolls-Royce Ltd.

Table 1 - Applications for Structural Adhesives in the RB 211

| ADHESIVE | MANUFACTURER | TYPE | APPLICATIONS |
|---|---|---|---|
| Redux 308 | CIBA-Geigy | Epoxy | Fan Casing (-22B, -524)<br>Acoustic Linings (-22B, -535, -524)<br>Blocker Door (-524) |
| Redux 319 | CIBA-Geigy | Epoxy | Thrust Reverser (-524)<br>Fan Casing (-535) |
| Redux 319A | CIBA-Geigy | Carried Epoxy | Hinged Side Panel (-22B) |

Epoxy adhesives (2) were chosen for a number of reasons which include:

a) Relative ease of bonding operations.

b) Quality control is well understood (3).

c) Many curing systems exist giving a wide range of adhesive properties.

d) Cure proceeds without the emission of volatiles.

e) Low shrinkage during cure.

f) Processing conditions are very 'forgiving'.

g) Cured epoxides are stable in most environments.

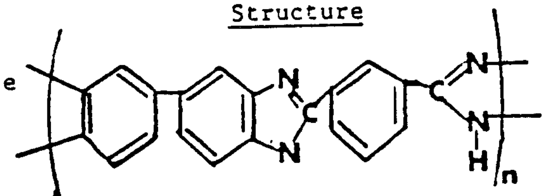
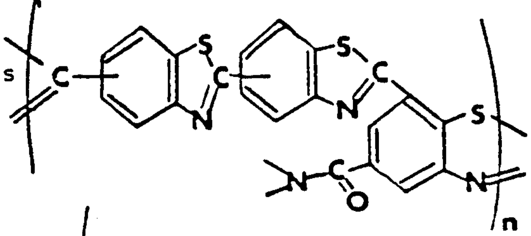
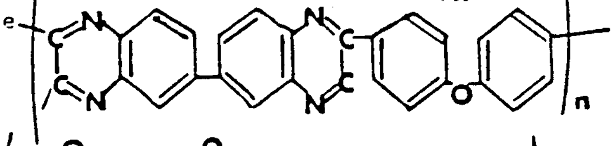
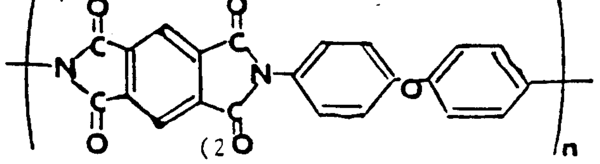
However, the most stable epoxy adhesives are limited to a maximum service temperature of about 180°C, by the nature of their molecular structure (2). In order to increase the application of composites to areas nearer to the hot core of an aircraft engine installation, composites and adhesives capable of surviving exposure to temperatures up to 350°C are required. It is clear therefore that an entirely new class of polymer is required for use in higher temperature adhesive applications.

## Candidate Polymers

Several organic polymers (4) have been synthesised over the past decade which have excellent thermal stability at elevated temperatures in an air environment. Some of these polymers are polyheterocyclic-aromatic and their structures are illustrated in Table 2.

All of these polymers are difficult to synthesise and contain expensive and unusual precursor chemicals. High temperatures and pressures are required to process these intractable materials. For example, the minimum conditions required to form efficient adhesive bonds with PBI are 316°C and 1.4 MPa. Polyimides are the most widely investigated of these polymers and are considered to be very promising for use as high temperature adhesives. Their processing parameters, although considerably more exacting than those applicable to epoxy resins, are far more realistic with respect to 'state of the art' production technology than the other classes of polymer illustrated in Table 2.

Table 2 - Polyheterocyclic - Aromatic Polymers

| Polymer | Structure | Reference |
|---|---|---|
| Polybenzimidazole<br>PBI |  | (5) |
| Polybenzothiazoles<br>PBT |  | (6) |
| Polyphenyl quinoxaline<br>PPQ |  | (7) |
| Polyimide<br>PI |  | (8) |

## Possible Applications for High Temperature Adhesives at Rolls-Royce Limited

The application of composite materials and structural adhesives to aero engines (1) has been confined to the colder parts of the power-plant, i.e. specifically the outer casing of the RB 211 nacelle. This has enabled epoxy resins to be utilised since the maximum temperatures experienced are less than 150°C. For applications closer to the core, especially engine turbine fairings, temperatures increase beyond 150°C and, short term, may rise as high as 300°C - 350°C. The high temperature components under consideration for manufacture in polyimide/carbon composites will, if successful, form a significant part of the whole engine nacelle assembly. Suitable matrix resins are currently available in commercial quantities from several suppliers, but the development of adhesives with comparable thermal-oxidative stability and which can be processed to give uniform bond strength is at an earlier stage.

## High Temperature Polyimide Matrix Resin (for composite structures)

A NASA developed resin, termed PMR-15 (9), has shown itself to be highly processable and high temperature resistant. This novel class of polyimides uses the in situ Polymerisation of Monomeric Reactants and can be processed into high quality, essentially void free components by either compression or autoclave moulding techniques (10).

In-house work has shown that this material will retain a high proportion of its original flexural strength for 5000h at 250°C, 2000h at 275°C and 1000h at 300°C (continuous exposure).

Table 3 - The Thermal Aging In Air of PMR-15/Satin Weave Carbon Fabric Composites at 250°C, 275°C and 300°C

| | % RETENTION IN FLEXURAL STRENGTH WITH RESPECT TO RT DATUM | | | |
|---|---|---|---|---|
| | RT | 250°C | 275°C | 300°C |
| DATUM | - | 96 | 84 | 78 |
| 5000h at 250°C | 83 | 75 | - | - |
| 2000h at 275°C | 85 | - | 78 | - |
| 1000h at 300°C | 72 | - | - | 57 |

RT Flexural strength = 1080 ± 50 MPa
All results comprise five test results.
Tested at 20:1 Aspect Ratio with a cross-head speed of 0,1 cm/min.
Thickness 1.37 mm. Construction 4 layers - 8 Harness Satin Weave

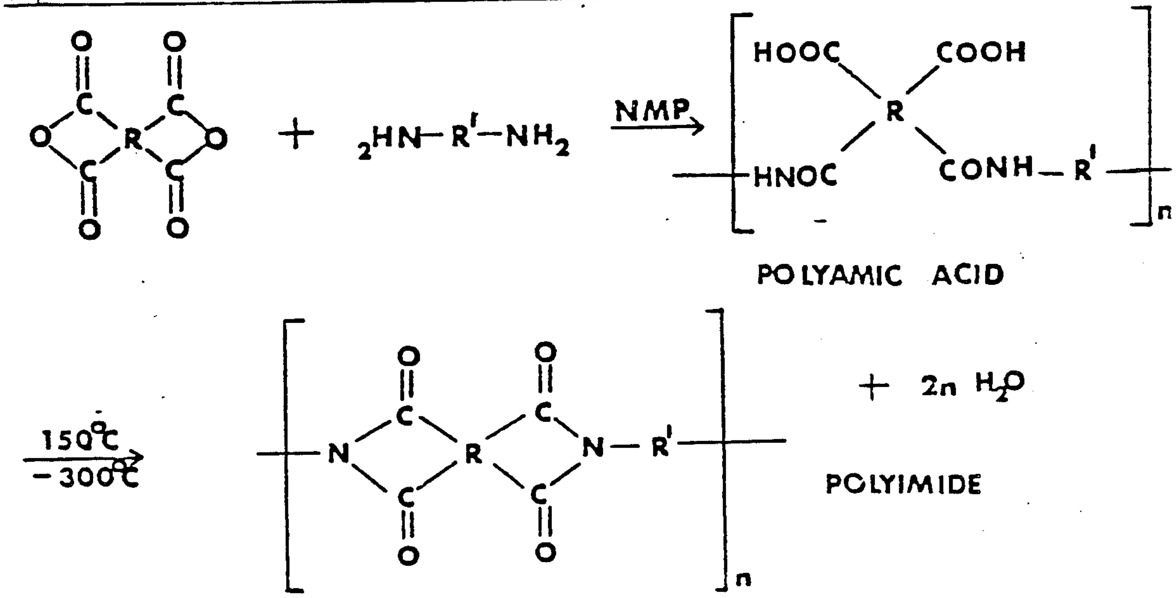
## Polyimide Adhesives - Cure Chemistry

Polyimide adhesives fall broadly into two classes; condensation and addition types.

### Condensation Polyimides

Condensation polyimides usually consist of a polyamic acid, intermediate prepolymer which is soluble in a strongly associating solvent such as N-methyl-2-pyrrolidone. The reaction path is outlined in Figure 1. Conversion of the polyamic acid to the polyimide is usually obtained by heating at 150°C to 300°C.

Figure 1 - Condensation Polyimides - Cure Chemistry

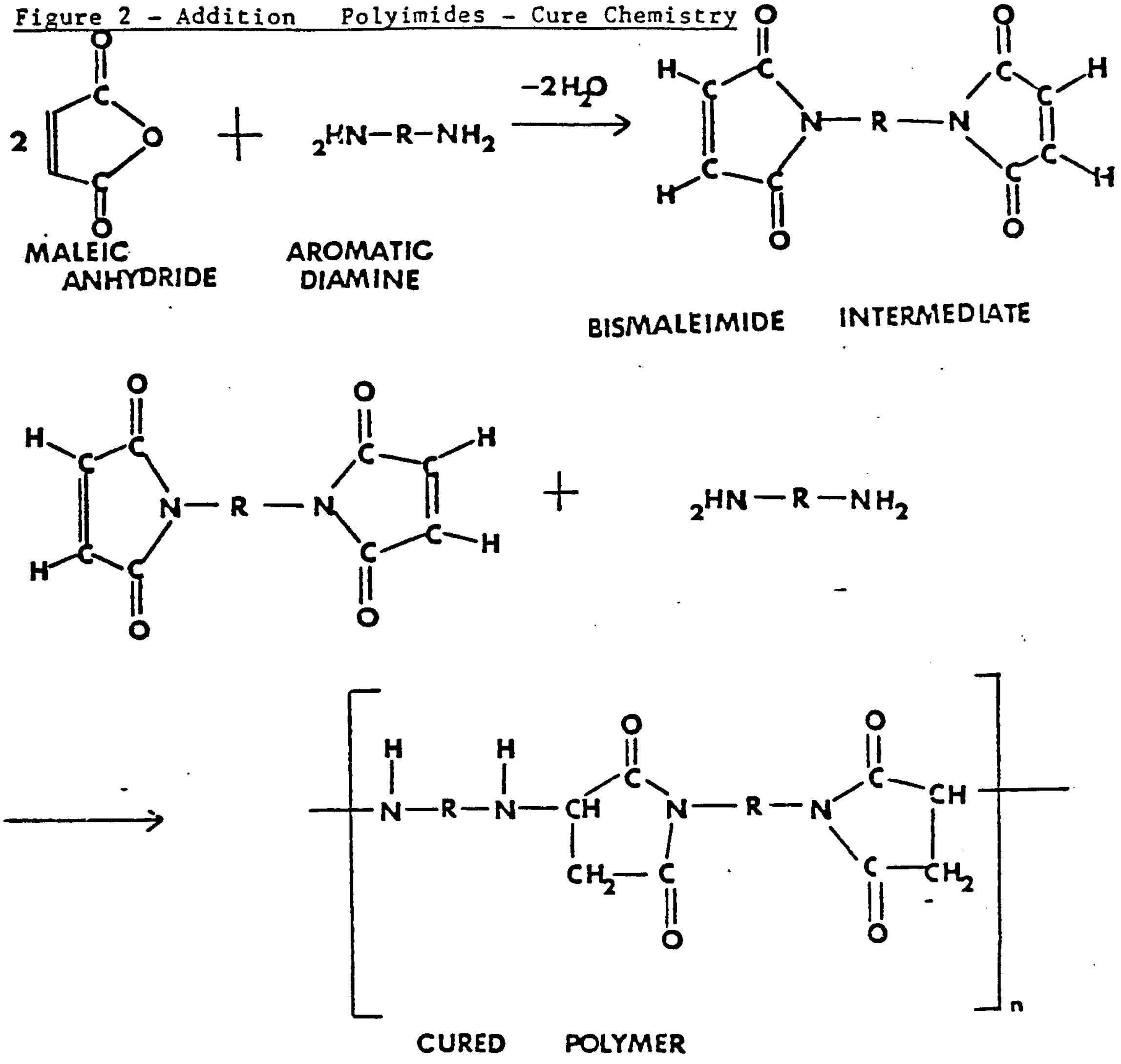


Water released during cyclodehydration always produces a voided glue line and limits the size of the area which can be bonded.

### Addition Polyimides

Recent work has resulted in the development of end-capped oligomers which can be cured by an addition reaction (<u>without</u> the evolution of volatiles) to produce a modified polyimide. A typical end cap is the maleimide group. The resulting intermediates are termed bismaleimides and final cure to polyimides occurs by addition through the double bonds which terminate the prepolymer or Michael reaction of excess amine with this double bond. The oxidative-thermal stability of the final polyimide suffers, however, as a result of the presence of aliphatic groups. The cure chemistry of Bismaleimides is illustrated in Figure 2.

Figure 2 - Addition Polyimides - Cure Chemistry



In order to improve thermal-oxidative stability, other 'end caps' (e.g. nadic (11) or acetylenic (12) groupings) have been incorporated into intermediate prepolymers. In this way, addition polyimide adhesives having comparable stability to the traditional condensation products have been established as viable formulations.

Table 4 compares and contrasts condensation and addition polimides.

Table 4 - A Comparison of the Characteristics of Condensation and Addition Polyimides

| CONDENSATION | ADDITION |
|---|---|
| • Precursor polyamic acids are hydrolytically unstable. | • Intermediate oligomer very stable at RT i.e. longer shelf life. |
| • Water released during cure produces a voided final polymer. | • No volatiles are released during cure giving a void free final polymer. |
| • Melt flow poor. | • Adequate melt flow. |
| • Thermal stability of final polymer is excellent | • Reduced thermal stability of final polymer |

## Currently Available Polyimide Adhesives

Table 5 describes the polyimide adhesives that are currently under development for use in the aerospace industry. Typical of their classes are FM34, (13), a condensation polyimide, and A7F (16), an addition polyimide. These adhesives will be discussed in more detail in later sections. Bismaleimide adhesives have not been included in Table 5. Production of the earlier bismaleimide adhesives was discontinued,but recently, interest has been revived and new formulations are currently under investigation (19). This class of adhesives will have inferior thermal-oxidative stability when compared to the truly aromatic polyimides.

### FM 34B-18

This adhesive consists of a polyamic acid filled with aluminium powder and supported on 112 style glass cloth. This condensation polyimide system has been in existence for many years and its main disadvantage is the evolution of volatiles during cure leading to a badly voided glue line. Also, in the uncured state, the precursor is affected by atmospheric moisture and final strength properties can be reduced significantly by such exposure.

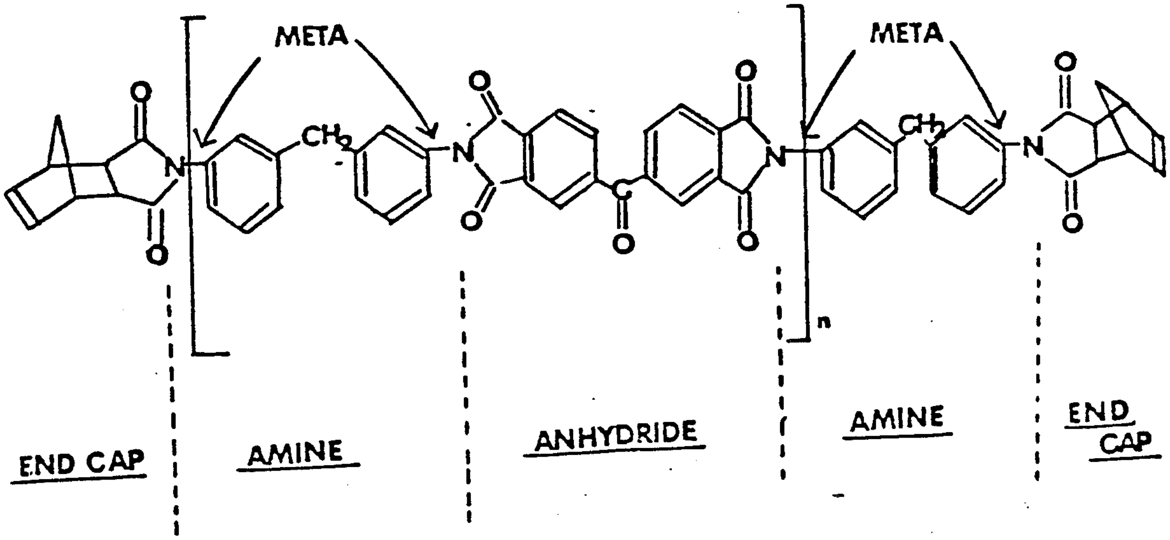
### A7F

In recent years, attempts have been made to synthesise prepolymers which have the very stable polyimide structure but can be polymerised via end groups which are capable of addition reactions.

Various addition polymers have been synthesised and, of these, the most promising termed LARC 13, was developed by NASA at the Langley Research Centre. This has the structure illustrated in Figure 3.

| ADHESIVE | FORM | SUPPLIER | TYPE | OTHER COMMENTS | REFERE |
|---|---|---|---|---|---|
| FM34B-18 | FILM & PASTE (BR34-18) | CYANAMID | CONDENSATION | •COMMERCIALLY AVAILABLE. | 13 |
| FM-36 | SUPPORTED FILM & PASTE(BR-36) | CYANAMID | CONDENSATION | •'IMPROVED' VERSION OF FM34.<br>•DEVELOPMENT QUANTITIES ONLY. | 14 |
| HP956<br>HP976 | FILM & PASTE | HEXCEL | CONDENSATION | •DEVELOPMENT QUANTITIES ONLY. | 15 |
| LARC 13 | PASTE | GULF | ADDITION | •NADIC END CAP. DEVELOPMENT QUANTITIES ONLY.<br>•SUPPLY DIFFICULTIES AND EXPENSIVE. | 16 |
| A7F | FILM & PASTE | US POLYMERIC | ADDITION | •DEVELOPMENT OF LARC 13 BY BOEING CAC.<br>•THERMOPLASTIC ADDITIVE.<br>•EXPENSIVE AMINE. | 16 |
| XA965-50 | FILM | US POLYMERIC | ADDITION | •CHEAPER AMINE USED.<br>•IN HOUSE DEVELOPMENT OF LARC13 EQUIVALENT. | - |
| EX335 | PASTE | HEXCEL | ADDITION | •CHEAPER AMINE USED.<br>•IN HOUSE DEVELOPMENT OF LARC 13 EQUIVALENT. | - |
| LARC TPI | FILM | GULF | THERMO-PLASTIC | •THERMOPLASTIC POLYIMIDE DEVELOPED BY NASA LANGLEY. | 17 |

Figure 3 - The Chemical Structure of LARC 13



The development of this adhesive is described in reference 18. In this work, various prepolymers were synthesised using different anhydrides and amines and their adhesive strengths were compared. The major finding was the dependence of joint strength upon the position of attachment of the amine group to the benzene rings. Adhesive strengths were always higher when the amine groups were situated in the meta $(3,3^1)$ position as opposed to the para $(4,4^1)$ position. The meta linkages allow processing between 533K and 598K because of the relatively low polymer softening temperature. The amine isomer effect far outweighed any changes in flexibilising group between benzene rings.

The formulation of this polymer into an optimised adhesive has been achieved by Boeing CAC. The adhesive, named A7F, has been well investigated and shows great promise as a structural adhesive at elevated temperatures.

The wider application of this adhesive has been delayed because the amine $(3,3^1$ Methylene DiAniline) required for synthesis is very expensive. The commercial production of this amine is currently under review by the manufacturers and NASA.

Cure Conditions

Typical cure parameters for A7F and FM 34 are described in Table 6 in which a comparison with a typical epoxy cycle is provided. In order to bond successfully with polyimide adhesive an autoclave cure must be applied. These adhesives require the use of high temperatures and pressures.

TABLE 6 CURE CYCLES OF VARIOUS ADHESIVES

| ADHESIVE TYPE | HEAT UP RATE (°C/MIN) | MAXIMUM CURE TEMPERATURE (°C) | VAC APPLIED | PRESSURE APPLIED (MPa) | TOTAL CURE TIME (hr) | OTHER COMMENTS |
|---|---|---|---|---|---|---|
| EPOXY | 1-3 | 175±5°C | FULL | 0,1-0,7 | 4 | MOST ADHESIVES MAY BE VAC. CURED ONLY |
| FM34B-18 CONDENSATION POLYIMIDE | 1,5-6 | 285-330 | FULL | 0,3 | 4-6 | SMALL BOND AREA ONLY |
| A7F ADDITION POLYIMIDE | 2-3 | 330 | FULL | 0,3-1,4 | 15 | EXTENSIVE B STAGING REQUIRED |

The provision of special accessory materials; vacuum bags, edge sealants, release films etc. capable of successful application at temperatures over 300°C is mandatory. Such materials are available but are expensive and will remain so until usage increases.

An autoclave capable of achieving the very high cure temperatures represents a considerable capital investment and only two suitable installations exist at this time in the UK.

## Adhesive Properties

For the purposes of comparison, the initial investigation of high temperature adhesives at Rolls-Royce Limited was based upon the use of Jethete (M152, 12% Chromium Ferritic Steel, HT to BHN 286-321) adherends. The thermal stability of this alloy, combined with its simple surface preparation make it a suitable vehicle for an initial investigation of adhesives.

### 'As Cured'

A comparison of shear strengths, based on the use of a double overlap shear test piece in Jethete, is provided in Figure 4. Shear strength is plotted against test temperature up to a maximum of 300°C and the superior retention of strength at high temperature displayed by the polyimides is clearly shown.

### 'Thermally Aged'

The superior thermal-oxidative resistance of polyimide adhesives is clearly shown in Table 7. After 1000h at 250°C, joints bonded with FM34 showed an increase with respect to datum hot strength.

After only 120h, epoxy joint strength had deteriorated to 34% retention of original hot strength.

FM34 adhesive has a useful life at 250°C measured in thousands of hours.

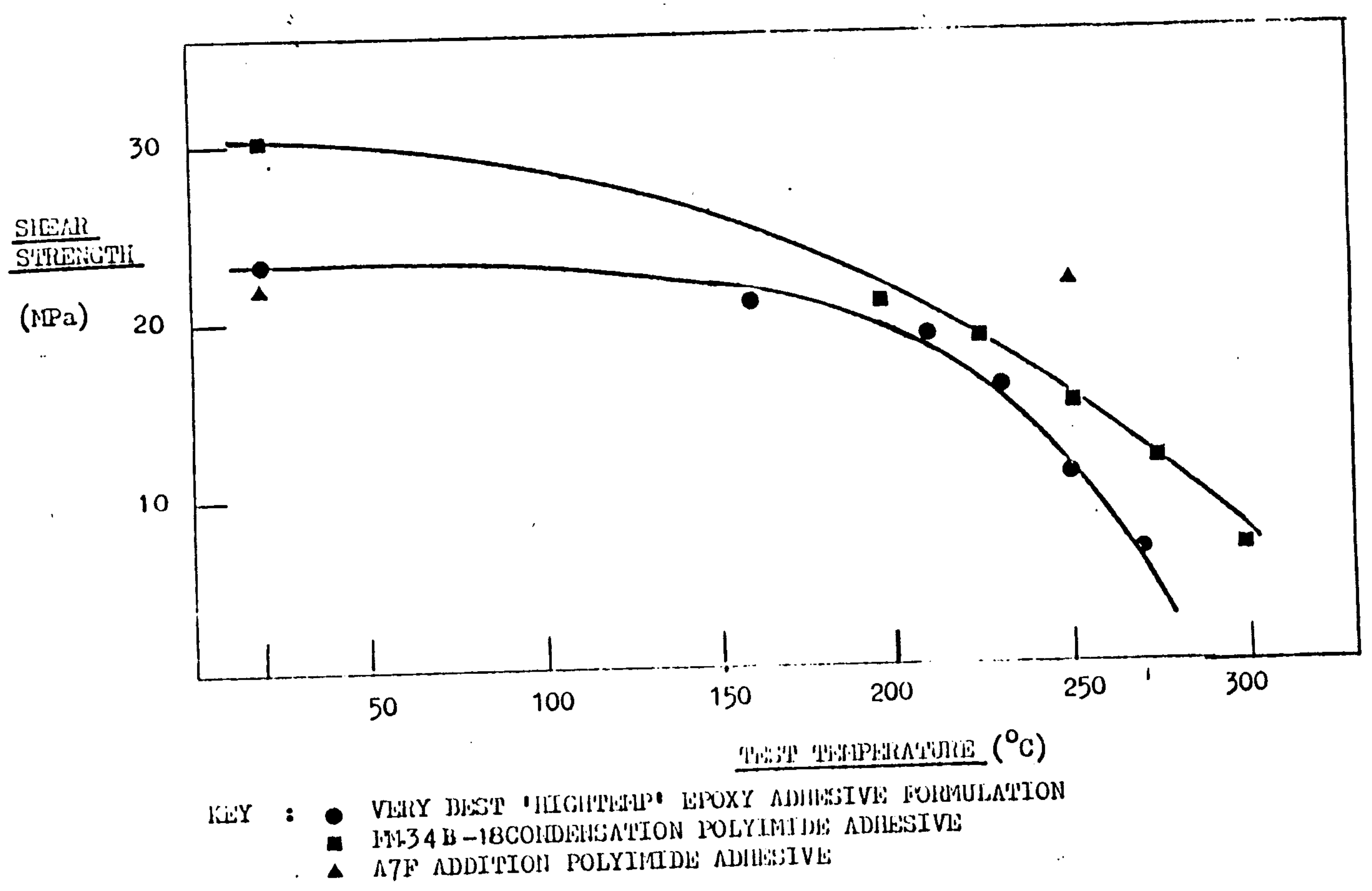
Table 7 - A Comparison of the Aging Characteristics of Jethete to Jethete Double Lap Joints Bonded with FM 34B-18 Polyimide Adhesive and a Typical Epoxy Adhesive

| Adhesive | (h) Aging Temp. | (°C) Aging Temp. | % Retention of RT Datum Shear Strength | % Retention of At Temp. Shear Strength |
|---|---|---|---|---|
| FM 34 | 1000 | 250 | 60 | 114 |
| Epoxy | 120 | 250 | - | 34 |
| FM 34 | 1000 | 275 | 32 | 99 |

### Surface Preparation

a) Vapour degrease with Genklene.
b) Lightly blast with 110-220 grit.
c) Vapour degrease and bond within 8h.

FIGURE 4 : A GRAPH OF SHEAR STRENGTH (DOUBLE LAP SHEAR JOINTS - JETHETE ADHERENDS) AGAINST TEST TEMPERATURE FOR VARIOUS ADHESIVES.



## Final Comments

Epoxy adhesives exist as a wide range of curing systems, whereby the end properties of variants may be tailored to a particular end usage, i.e. toughened formulations having excellent peel strength are readily available.

Polyimide adhesives, however, normally exist as hard, brittle materials when cured, yielding high shear strengths but very low peel strengths. One aim in the development of A7F has been to improve peel characteristics by incorporation of high temperature thermoplastics. Further development of formulations is still required.

The manufacture of a thermoplastic polyimide resin (LARC TPI) by NASA Langley (17) may further improve the situation, but the adhesive is at an early stage of investigation.

## Summary

The salient features of polyimide adhesives can be summarised as follows:

a) Very stable structure with excellent thermal oxidative stability.

b) Addition polyimides may be cured to give void free glue lines.

c) High temperatures are required for processing.

d) Special accessory materials are necessitated.

e) Available only in development quantities.

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