NASA TM- 83172

NASA Technical Memorandum 83172

NASA-TM-83172 19810022817

THE EFFECT OF ELASTOMER CHAIN LENGTH ON PROPERTIES OF SILICONE-MODIFIED POLYIMIDE ADHESIVES

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AUGUST 1981

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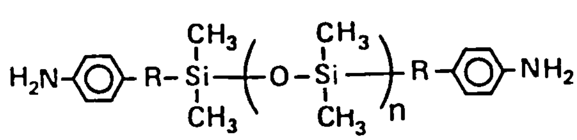
INTRODUCTION

Because of their thermal stability and easy processability, addition polyimides are candidate high-temperature adhesives for bonding composite materials and metals such as titanium on future aircraft and spacecraft. An addition polyimide adhesive developed at NASA-Langley Research Center, LARC-13, is currently being used for bonding an experimental graphite/polyimide composite wing panel on the NASA YF-12 aircraft.[1-3] LARC-13 is a thermoset material which cures by an addition reaction involving unsaturated nadimide end groups. As is typical of a thermoset, the fully-cured LARC-13 polymer is highly crosslinked, insoluble, and extremely brittle. In order to broaden the applicability of LARC-13 as an adhesive, a method for toughening this material is needed to improve such properties as peel and adhesive fracture resistance.

A recent study was conducted at NASA-Langley which involved the incorporation of various silicone and butadiene/acrylonitrile elastomers into the addition polyimide adhesive LARC-13.[4] Incorporation of elastomer particles at a concentration of 15% solids by weight resulted in a 6 to 7-fold increase in peel strength and a 3 to 5-fold increase in the fracture toughness of LARC-13. This improvement in toughness was accomplished at a sacrifice in the elevated temperature adhesive strength of the material. However, the high-temperature strengths of LARC-13 adhesives prepared with silicone elastomers significantly improved after aging at 232°C for 500 hours.

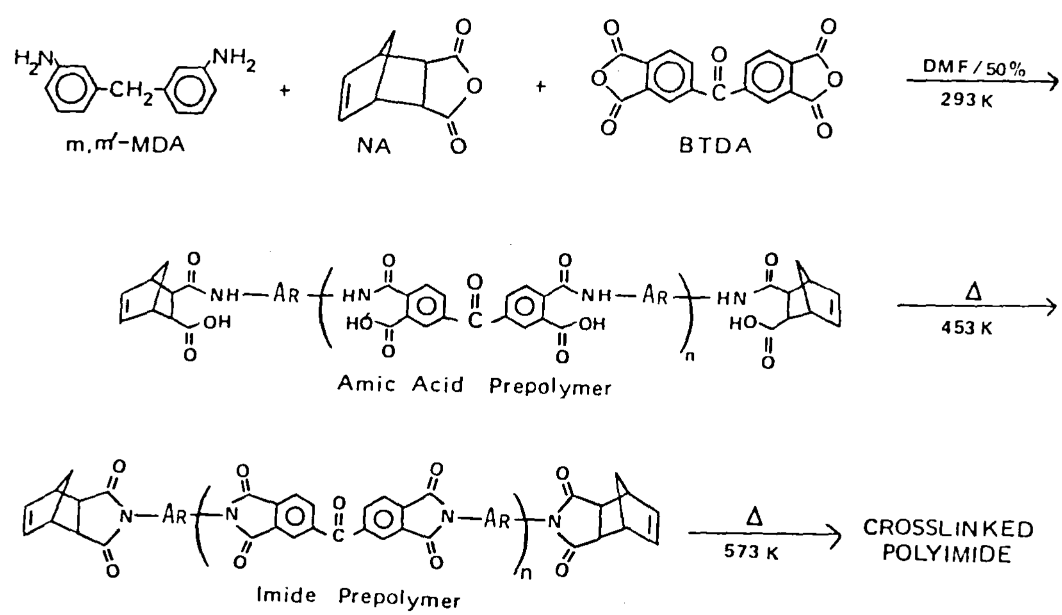
In an effort to optimize properties of silicone-toughened LARC-13, a new series of polymers has been synthesized using several amine-terminated silicone elastomers which contain varying chain lengths. The aromatic amine-terminated silicone (ATS) shown below prepared with chain lengths varying from n=10 to n=105 were reacted into the backbone of LARC-13 in order to observe the effect of elastomer chain length on polymer properties.



SYNTHESIS OF ADHESIVES

The synthetic route for preparing LARC-13[2], which was used as a control throughout this study, is shown below. Appropriate quantities of m,m'-methylenedianiline (m,m'-MDA), nadic anhydride (NA), and 3,3'4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) are combined in an amide solvent at a concentration of 50% solids by weight to form a 1300 molecular weight amic acid. This amic acid prepolymer is used as the adhesive resin and is later cured to the crosslinked polyimide by removal of solvent, imidization, and bonding under pressure at 300°C.

The rubber-modified LARC-13 resins were prepared by chemically incorporating aromatic amine-terminated silicones (ATS) with varying chain lengths into the LARC-13 backbone. The ATS elastomers were obtained as low viscosity liquids from Bergston and Associates, Schenectady, New York. Each elastomer was substituted for a portion of the MDA diamine so that the elastomer concentration was equal to 15% by weight of the total solution solids. The ATS elastomers were dissolved in dimethylformamide (DMF) by stirring at room temperature in the reaction vessel. The remaining MDA was added to the elastomer solution followed by the anhydride monomers. The ATS-modified resins were stirred overnight and refrigerated.

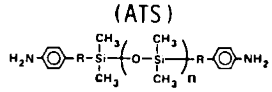


ADHESIVES CONTAINING AMINE-TERMINATED SILICONES

As shown in the top half of the table below, four formulations of LARC-13/ATS were prepared with a 15% elastomer content and chains containing 10, 41, 63, and 105 repeat units. Brookfield viscosities of the polyamic acids were measured at 23°C and 12 rpm. The addition of the four ATS elastomers to LARC-13 caused a reduction in the amic acid viscosity. This phenomenon which has been previously observed[4] was especially pronounced for the polymer containing ATS_{10}.

Three additional LARC-13/ATS formulations were prepared (bottom half of table) using a 50:50 combination of ATS elastomers having repeat units of 105 and 10. These resins containing a combination of two elastomers were made at three elastomer concentrations of 8, 15 and 25% w/w solids. These bimodal formulations were of interest because of a previous study on epoxies which resulted in an enhancement of properties when the polymers were modified with bimodally distributed elastomer particles.[5] A significant drop in the Brookfield viscosity of these resins was observed as the elastomer content was increased from 8 to 25%. This may be due to an offset in the monomer stoichiometry due to elastomer impurities or the presence of small amounts of water in the elastomers.

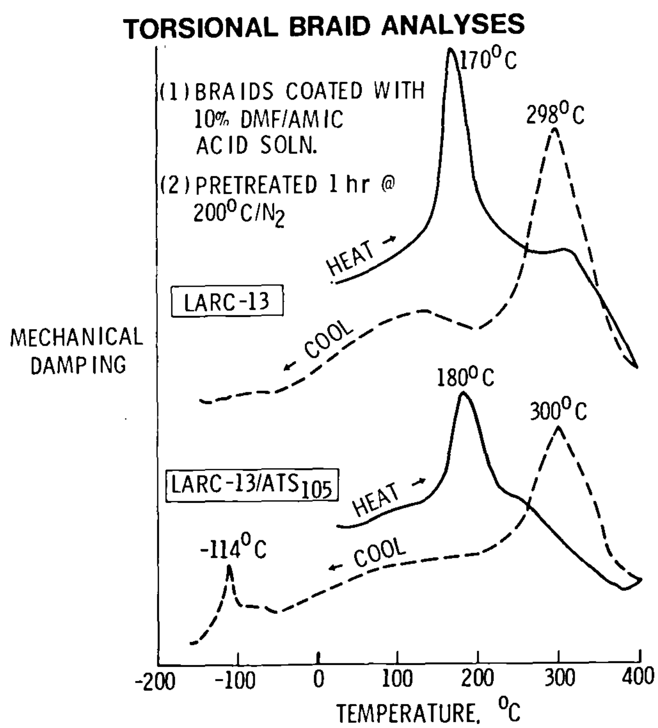
LARC-13 ADHESIVES CONTAINING AMINE-TERMINATED SILICONES

ADHESIVE	ELASTOMER STRUCTURE (ATS) 	ELASTOMER CONCENTRATION %	BROOKFIELD VISCOSITY (cps)
LARC-13	NONE	0	2300
LARC-13/ATS_{105}	n = 105	15	1675
LARC-13/ATS_{63}	n = 63	15	1900
LARC-13/ATS_{41}	n = 41	15	1750
LARC-13/ATS_{10}	n = 10	15	1350
LARC-13/ATS_{105} + ATS_{10}	n = 105, n = 10 (50:50)	8	1850
LARC-13/ATS_{105} + ATS_{10}	n = 105, n = 10	15	680
LARC-13/ATS_{105} + ATS_{10}	n = 105, n = 10	25	490

THERMOMECHANICAL PROPERTIES OF ATS-MODIFIED POLYIMIDES

Thermomechanical properties of the LARC-13/ATS resins were obtained by torsional braid analysis (TBA). Glass braids were coated with a 10% DMF solution of the polyamic acid prepolymers and then heated in a nitrogen oven for 1 hour at 200°C to complete imidization. TBA data was recorded on heating the pretreated braids at 3°C/min. in a nitrogen atmosphere from room temperature to 400°C and by cooling from 400°C to cryogenic temperatures.

TBA curves of LARC-13 and LARC-13/ATS_{105} are compared below. The curve displayed for the LARC-13/ATS_{105} polymer was typical in appearance of all the ATS-modified polymers tested. Upon heating from room temperature, the LARC-13 control showed a melt of the imide prepolymer at 170°C (solid line) followed by a distinct glass transition temperature (T_g) at 298°C obtained by cooling the polymer braid from 400°C (dotted line). Similar behavior was noted for the ATS_{105}-modified LARC-13 except for the presence of a peak at -114°C due to the elastomer.



TBA DATA ON ATS-MODIFIED POLYIMIDES

Torsional braid analysis data on all of the ATS-modified polymers with an elastomer content of 15% w/w are shown in the table below. Melt temperatures of the imide prepolymers ranged from 176°-186°C. Two transitions were displayed by all of the cured ATS-modified resins; a T_g of the LARC-13 phase was present at high temperature (293° to 318°C) and a distinct elastomer T_g was evident at low temperature (-119° to -113°C). The T_g values of the neat elastomers (as received from the manufacturer) with no thermal history were recorded by cooling from room temperature and are listed in the last column of the table. T_g values of elastomers having repeat units of 41, 63, and 105 increased upon incorporation into LARC-13 and curing to 400°C. This increase in the T_g of silicone elastomers after curing is indicative of crosslinking[6] and has been previously observed.[4] The reason for the reduction in the T_g of ATS_{10} after incorporation into LARC-13 is not yet understood. A glass braid coated with a 50:50 mixture of neat ATS_{105} and ATS_{10} elastomers displayed T_g peaks at -97° and -128°C, the same for the individual elastomers. However, upon curing with LARC-13, these bimodally distributed elastomers produced only a single peak at -119°C which falls between the two values observed for the two elastomers.

TORSIONAL BRAID ANALYSIS DATA ON ATS-MODIFIED POLYIMIDES

POLYMER	PREPOLYMER MELT[a] (°C)	POLYMER[b] T_g (°C)	ELASTOMER[b] T_g (°C)	NEAT ELASTOMER[c] T_g (°C)
LARC-13	170	298	NONE	NONE
LARC-13/ATS_{105}	180	300	-114	-128
LARC-13/ATS_{63}	181	318	-113	-126
LARC-13/ATS_{41}	186	302	-116	-125
LARC-13/ATS_{10}	179	293	-113	-97
LARC-13/ ATS_{105}+ATS_{10}	176	301	-119	-128;-97

[a] PREPOLYMER HEATED FROM RT
[b] DETERMINED BY COOLING POLYMER FROM 400°C
[c] ELASTOMER (AS RECEIVED) COOLED FROM RT

ADHESIVE BONDING

The ATS-modified LARC-13 amic acids were prepared for adhesive bonding by adding 30% w/w aluminum powder (325 mesh) filler. Adhesive carrier cloths were then prepared by brush-coating each resin onto 112 E-glass (A-1100 finish) cloths which were tightly stretched over aluminum frames. The scrim cloths were dried between coats in forced air for 1/2 hour at 60°C, and after the final fourth coat for 1 hour at 100°C and 1/2 hour at 180°C.

Simultaneously, 6Al-4V titanium adherends were prepared for bonding. The bonding area was cleaned using the Pasa Jel 107 acid surface treatment, primed with adhesive, and heated in air for 1 hour at 100°C. The adhesive-coated scrim cloths were then sandwiched between adherends with a 1.27 cm overlap and bonded according to the bonding cycle presented below. Lap shear tests were performed on an Instron Testing Instrument according to ASTM D-1002 at a crosshead speed of 0.127 cm/min. Elevated temperature tests were conducted after soaking the specimens for 10 min. at the test temperature.

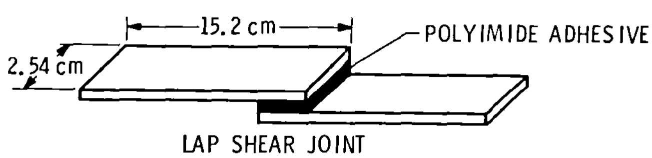
BONDING PROCESS FOR POLYIMIDE ADHESIVES

(1) CARRIER CLOTH: E-GLASS/A1100 CLOTH COATED WITH ADHESIVE + 30% Al POWDER; B-STAGED AT 180°C FOR 30 min

(2) TITANIUM ADHERENDS: PASA JEL CLEANED; PRIMED WITH 2 COATS ADHESIVE AND HEATED 1 hr AT 100°C

(3) BONDING: ADHESIVE CLOTH SANDWICHED BETWEEN ADHERENDS WITH A 1.27 cm OVERLAP AND BONDED

- RT → 300°C & HOLD 30-45 min
- APPLY 345 KPa (50 psi) & HOLD 30 min
- COOL TO RT UNDER PRESSURE



LAP SHEAR JOINT

EVALUATION OF ATS-MODIFIED ADHESIVES

Adhesive lap-shear strengths of ATS-modified LARC-13/titanium bonds tested at both ambient and elevated temperatures are presented in the table below. Each number in the table represents an average lap-shear strength of four individual specimens. Relative deviations in lap-shear strengths were approximately 7% for unaged specimens and 4% for those aged at 232°C. All failures were cohesive.

Toughening is generally achieved at the expense of elevated temperature properties.[6] This proved to be the overall case for those LARC-13 formulations containing individual elastomers ATS_{10} to ATS_{105}. Elevated temperature lap-shear strengths of unaged ATS-modified LARC-13 adhesives were consistently lower than for the LARC-13 control resin. These adhesives, like LARC-13, did improve in strength after aging at 232°C which is indicative of a post-cure effect. The most surprising results of this study, however, were the excellent strengths displayed by the LARC-13 forumulation containing the 50:50 bimodal distribution of elastomers ATS_{105} + ATS_{10}. The strengths of the unaged polymer were equivalent to those of LARC-13 at RT and 288°C, but lower at 232°C and 260°C. After aging at 232°C, the LARC-13/ATS_{105} + ATS_{10} bonds exhibited improved strengths over those adhesives containing individual elastomers but lower than those of LARC-13.

ADHESIVE	LAP SHEAR STRENGTH, psi UNAGED SAMPLES				LAP SHEAR STRENGTH, psi AGED 500 hrs @ 232°C			
	RT	232°C	260°C	288°C	RT	232°C	260°C	288°C
LARC-13	2850	2800	2130	1280	2920	2910	2480	2160
LARC-13/ATS_{105}	2550	1800	1130	870	1710	1630	1620	1390
LARC-13/ATS_{63}	2550	1380	1030	700	1580	1550	1640	1320
LARC-13/ATS_{41}	2480	1770	1430	805	1710	1630	1600	1410
LARC-13/ATS_{10}	2910	1850	1150	690	1810	1670	1650	1430
LARC-13/ ATS_{105} + ATS_{10}	3000	2070	1850	1300	2300	1930	1910	1720

*ADHESIVES FILLED 30% WITH ALUMINUM POWDER

EFFECT OF ELASTOMER CONCENTRATION ON ADHESIVE STRENGTH

In the evaluation of ATS-modified adhesives, LARC-13/ATS_{105} + ATS_{10} was found to have the highest lap shear strength and best retention of strength after aging of all the formulations tested. The concentration of the bimodally distributed elastomers in LARC-13 was then varied in order to find the concentration which would maximize the adhesive properties of this material.

As shown in the table below, concentrations of 8, 15, and 25% solids by weight of the elastomers were incorporated into the LARC-13 adhesive. The adhesive prepared with 15% elastomer concentration exhibited the best lap-shear strengths before and after aging. This is an interesting finding in view of previous work which proved that a 15-20% concentration of elastomer particles provided maximum properties for certain epoxies(6).

EFFECT OF ELASTOMER CONCENTRATION ON LARC-13/ATS_{105} + ATS_{10} ADHESIVE STRENGTHS

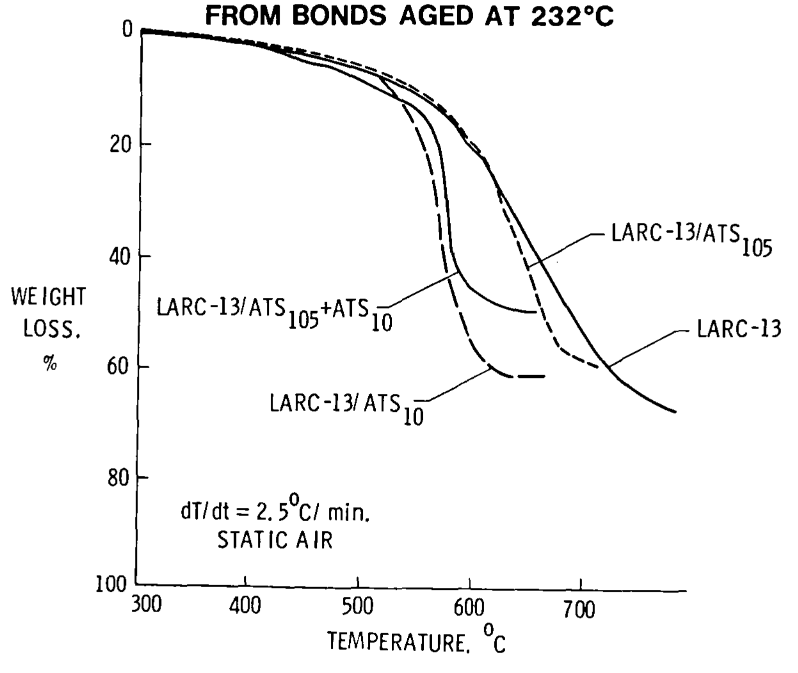
ELASTOMER CONCENTRATION %	INITIAL LAP SHEAR STRENGTH, psi		LAP SHEAR STRENGTH, psi AFTER 500 hrs@ 232^{0}C	
	RT	288^{0}C	RT	288^{0}C
0	2850	1280	2920	2160
8	2500	950	1670	1450
15	3000	1300	2300	1720
25	2890	830	1840	1340

THERMOGRAVIMETRIC ANALYSIS OF ATS-MODIFIED POLYIMIDES

Thermogravimetric analyses (TGAs) of adhesive flash (excess adhesive flow extracted from lap-shear bondlines) were performed in static air at a heating rate of 2.5°C/min. The dynamic TGA curves of several adhesives aged at 232°C for 500 hours are presented in the figure shown below.

All of the adhesives tested were similar in thermal stability with an approximate 10% weight loss at 500°C. Between 500° and 700°C, the LARC-13 and LARC-13/ATS_{105} were the most thermally stable, with the latter only slightly less stable than the control material. The LARC-13/ATS_{10} containing the silicone elastomer with the shortest chain length was lowest in thermal stability. Thermal decomposition of the LARC-13 containing 50:50 ATS_{105} + ATS_{10} fell somewhere in between those polymers containing the individual elastomers.

THERMOGRAVIMETRIC ANALYSIS (TGA) OF ADHESIVE FLASH FROM BONDS AGED AT 232°C



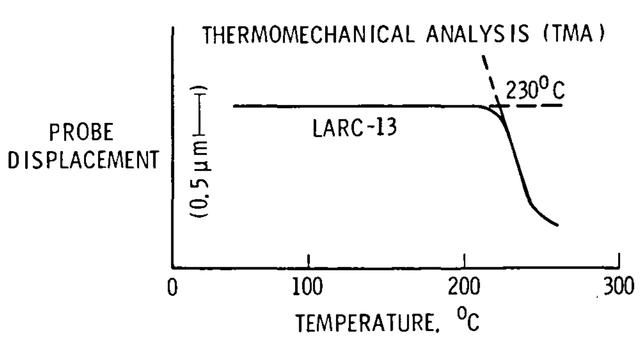
CHARACTERIZATION OF ADHESIVES BY THERMOMECHANICAL ANALYSIS

Thermomechanical analysis (TMA) was used as a method for measuring the softening or glass transition temperature (T_g) of flash taken from the adhesive bondlines before and after aging at 232°C. TMA curves like the one of LARC-13 shown in the figure below were obtained by heating the flash in static air at 5°C/min. under a 15g penetration probe.

The T_g of LARC-13 increased by 30°C after aging for 500 hours at 232°C indicating that this adhesive was not fully cured during the initial bonding process and continued to crosslink during aging. The adhesives containing silicone elastomers exhibited higher initial T_g values which increased very little if any after aging at elevated temperature. It is also interesting to note that the T_g of the adhesive containing 50:50 ATS_{105} + ATS_{10} elastomers was between those of the adhesives formulated with the individual elastomers.

SOFTENING TEMPERATURES OF ADHESIVE FLASH

ADHESIVE	T_g OF UNAGED FLASH (°C)	T_g OF FLASH AGED 500 hrs. @ 232°C (°C)
LARC-13	230	260
LARC-13/ATS_{105}	270	276
LARC-13/ATS_{10}	249	250
LARC-13/ATS_{105}+ATS_{10}	260	256



CONCLUSIONS

A study has been conducted to determine the effect of elastomer chain length on the properties of silicone-containing polyimide adhesives. A series of LARC-13 addition polyimide adhesives was synthesized by chemically reacting into the polymer backbone several aromatic amine-terminated silicones (ATS) with repeat units varying from n=10 to 105. An additional formulation was prepared which contained a bimodal distribution of elastomers having the highest and lowest repeat units (ATS_{105} + ATS_{10}).

All of the ATS-modified LARC-13 resins displayed a separate T_g for the elastomer phase at low temperature (-119° to -113°C) and a T_g at higher temperature (293° to 318°C) due to the LARC-13 phase. The addition of the individual ATS elastomers resulted in a sacrifice in the high-temperature adhesive strength of LARC-13. However, the resin prepared with a 50:50 combination of elastomers ATS_{105} + ATS_{10} exhibited much enhanced adhesive strengths. The lap-shear strengths of the unaged LARC-13/ ATS_{105} + ATS_{10} were equivalent to those of LARC-13; upon aging, the elevated temperature strengths of the LARC-13/ATS_{105} + ATS_{10} were midway between those of LARC-13 and the other resins containing individual elastomers. A concentration of 15% w/w elastomers was found to be the best for obtaining maximum ahesive strengths.

Flash from the adhesive bondlines were characterized by both thermogravimetric analysis (TGA) and thermomechanical analysis (TMA). Although the thermal stabilities of the resins determined by TGA were relatively close together, the LARC-13 and LARC-13/ATS_{105} proved to have the highest decomposition temperatures. T_g values of the adhesives were obtained by TMA, and results showed that LARC-13 was somewhat undercured during the bonding process in comparison to the elastomer-modified resins.

Results from this study have shown that variation of the elastomer chain length had very little effect on the properties of the ATS-containing LARC-13 adhesives. An important finding, however, was the great enhancement in elevated temperature adhesive strengths obtained by incorporating into LARC-13 equal amounts of elastomers containing long and short chain lengths. This material containing a bimodal distribution of elastomers shows much potential as an aerospace adhesive for selected high-temperature applications.

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1. Report No. NASA TM-83172	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle EFFECT OF ELASTOMER CHAIN LENGTH ON SILICONE-MODIFIED POLYIMIDE ADHESIVES		5. Report Date August 1981
		6. Performing Organization Code 505-33-33-02
7. Author(s) Anne K. St. Clair, Terry L. St. Clair and Stephen A. Ezzell		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address NASA-Langley Research Center Hampton, VA 23665		11. Contract or Grant No.
		13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546		14. Sponsoring Agency Code

15. Supplementary Notes

An oral presentation of this work will be given at the 33rd Southeastern Regional Meeting of the American Chemical Society, November 4-6, 1981 in Lexington, Kentucky.

16. Abstract

A series of polyimides containing silicone elastomers has been synthesized in order to study the effects of the elastomer chain length on polymer properties. The elastomer with repeat units varying from n=10 to 105 were chemically reacted into the backbone of an addition polyimide oligomer via reactive aromatic amine groups. Glass transition temperatures of the elastomer and polyimide phases were observed by torsional braid analysis. The elastomer-modified polyimides were tested as adhesives for bonding titanium in order to determine their potential for aerospace applications. Adhesive lap shear tests were performed before and after aging bonded specimens at elevated temperatures.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Polyimides Elastomers Adhesives	Unclassified-Unlimited Subject Category - 27

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	13	A02

N-305

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