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HIGH TEMPERATURE ADHESIVES FOR BONDING KAPTON[®]

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Abstract

Experimental polyimide resins have been developed and evaluated as potential high temperature adhesives for bonding Kapton* polyimide film. Lap shear strengths of "Kapton"/"Kapton" bonds were obtained as a function of test temperature, adherend thickness, and long term aging at 575K (575°F) in vacuum. Glass transition temperatures of the polyimide/"Kapton" bondlines were monitored by thermomechanical analysis.

1. INTRODUCTION

Very few adhesives exist that are suitable for long term use at elevated temperature. Commercially available high temperature adhesives have been formulated for bonding metals such as steel and titanium. However, these systems generally contain additives which make the resins too brittle for film bonding applications. A particular need for adhesives that are compatible with polyimide film such as "Kapton" (H-film) was recently introduced by the proposed NASA-Solar Sail Program. A successful adhesive for bonding film should form a flexible coating and be amenable to bonding

cycles which involve low pressure as well as very short time at the bonding temperature. The objective of this work was to develop a high temperature adhesive for bonding ultrathin polyimide "Kapton" film. Candidate adhesives for these applications will need to provide good performance in a space environment for long term at 575K.

One group of high temperature polymers which show promise as adhesives and possess the capability of forming flexible film coatings are the linear condensation polyimides, which are compatible with the linear polyimide "Kapton" film adherend.

Three promising polyimide LARC

*DuPont trademark, Reg. U. S. Pat. and Tm. Off.

adhesives^(1,2) prepared in the amic acid form in the aliphatic ether solvent, diglyme, were developed and studied along with a new experimental NR-150-B2X^(3,4) precursor adhesive prepared in amide solvent as a monomeric mixture.

2. EXPERIMENTAL

2.1 ADHESIVES

The monomers used in the preparation of the LARC adhesives were 3,3',-4,4'-benzophenone tetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and 3,3'- or 4,4'-diaminobenzophenone (DABP). The BTDA and PMDA were obtained commercially and purified by vacuum sublimation, (m.p. 497K and 558K respectively). The diamines were obtained from commercial sources and purified by recrystallization. The reagent grade bis(2-methoxyethyl) ether (diglyme) was used as received. The LARC-2 polyamic acid was prepared by reacting stoichiometric amounts of 3,3'-DABP (0.015 mole) and BTDA (0.015 mole) in 45g of diglyme at ambient temperature for 16 hours (Table 1). In a similar manner, the amic acid of LARC-3 was made by adding a 2:1 molar ratio of BTDA (0.010 mole)/PMDA (0.005 mole) to 3,3'-DABP (0.015 mole) in 42g of

diglyme. The amic acid of LARC-4 was prepared from a 3:1 ratio of BTDA (0.012 mole)/PMDA (0.004 mole) and 4,4'-DABP (0.016 mole in 46g of diglyme. Films were cast from the 15% solids amic acid solutions onto soda-lime glass plates and thermally cured by heating in a forced air oven for one hour at each of three temperatures, 373K, 473K and 573K. The LARC polyimide films thus formed, were then characterized. The remaining polyamic acid solutions were kept under refrigeration until needed for bonding. The experimental NR-150 precursor adhesive solution, NR-150-B2X, was obtained as a mixture of monomers at 48% solids (w/w) in N-methylpyrrolidone (NMP).⁽⁵⁾ The monomeric binder solution contained a 1.5% excess of the 2,2-bis-(3',4'-dicarboxyphenyl)hexafluoropropane dianhydride (6F) and a 3:2 ratio of paraphenylenediamine (PPD)/oxydianiline (ODA). The experimental NR-150-B2X solution was diluted from 48% to 32% with ethanol before coating adherends. A film of the monomeric NR-150-B2X solution was also cast from NMP/ethanol, cured and characterized.

2.2 CHARACTERIZATION

Inherent viscosities of the polyamic

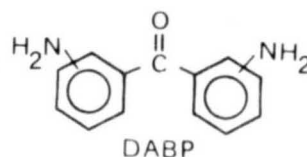
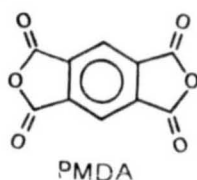
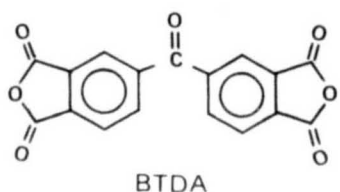


TABLE I. PROPERTIES OF ADHESIVES

Resin	Formulation	Amic Acid η_{inh}	T_g K (°F)
LARC-2	BTDA 3,3'-DABP	0.70	520 (477)
LARC-3	2 BTDA/1 PMDA 3,3'-DABP	0.63	542 (515)
LARC-4	3 BTDA/1 PMDA 4,4'-DABP	0.50	570 (567)
NR-150-B2X	6F(1.5% excess) 3 PPD/2 ODA	--	595 (612)

TABLE II. MECHANICAL PROPERTY DATA ON KAPTON ADHERENDS

Adherend Thickness	Test Temperature	Tensile Strength MPa (psi)	Yield Strength at 2% MPa (psi)	Elongation %	Tensile Modulus MPa (psi)
0.025 mm (1 mil)	RT	172 (24,900)	62 (9000)	35	2920 (424,000)
	575K	78 (11,300)	31 (4500)	55	1230 (179,000)
0.051 mm (2 mil)	RT	177 (25,700)	44 (6400)	84	2760 (400,600)
	575K	63 (9200)	24 (3500)	70	1040 (150,600)
0.076 mm (3 mil)	RT	163 (23,700)	50 (7200)	57	2500 (362,000)
	575K	71 (10,300)	26 (3700)	82	1120 (162,000)
0.127 mm (5 mil)	RT	179 (26,000)	50 (7300)	56	2890 (419,000)
	575K	74 (10,700)	26 (3800)	82	1350 (196,000)

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acid LARC resins were determined at a concentration of 0.5% in dimethylacetamide at 308K. The glass transition temperature (T_g) of each polyimide film was determined by differential scanning calorimetry (DSC) on a DuPont Model 990 Thermal Analyzer with the Standard DSC cell attachment at a heating rate of 20K/min. The T_g values of the adhesive bondlines were measured by thermomechanical analysis (TMA) in static air at a 5K/min. heating rate on a DuPont Model 943 Thermomechanical Analyzer. A 1/2 cm x 1/2 cm sample was cut from the adhesive bondline and mounted under the TMA quartz penetration probe loaded with a 20g weight.

2.3 ADHERENDS

The polyimide "Kapton" adherends were acquired from the Electrical Insulation Products Division, E. I. Du Pont de Nemours and Co. in the following thicknesses: 0.025 mm (1 mil), 0.051 mm (2 mil), 0.076 mm (3 mil) and 0.127 mm (5 mil).

"Kapton" panels measuring 11.4 cm (4.5 in) x 15 cm (6 in) were cut from the film rolls with the 15 cm dimension in the longitudinal direction. No surface preparation of the film was required other than the removal of fingerprints, dust, etc. with ethanol when necessary. The tensile properties of the "Kapton" adherends were obtained on film strips 2.54 cm (1 in) wide and are shown in Table II. The majority of adhesive screening was performed

with the 0.051 mm (2 mil) "Kapton". Whenever bonding with the thinner "Kapton" was attempted, 50% of the failures occurred in the adherend itself rather than in the adhesive bondline. Therefore, to obtain consistent adhesive strengths, films 0.051 mm (2 mil) or thicker were bonded.

2.4 BONDING PROCESS

"Kapton" film panels were brush coated 0.64 cm (1/4 in.) from the edge with either the LARC polyamic acid solutions in diglyme or the NR-150-B2X in NMP/ethanol. The coated adherends were B-staged 1 hour at 373K and 1/2 hour at 448K in a forced air oven. Each primed panel was then overlapped 0.64 cm (1/4 in) with an unprimed panel and bonded at 616K (650°F) with a hot iron for 20 seconds. Only contact pressure of the iron on the bondline was necessary for bonding. Final bondline thicknesses ranged from 0.008 mm (0.3 mil) to 0.013 mm (0.5 mil).

2.5 VACUUM AGING

Prior to vacuum aging, each bonded film specimen was cut into four 2.54 cm (1 in.) strips and a small hole was punched at the top of each panel for mounting in the vacuum oven (see Figure 1). Sets of specimens were aged isothermally at 575K in vacuum and removed for testing after 250, 500, 1000, 1500, 2000, and 3000 hours. Samples were mounted on metal racks down the center of a

vacuum chamber measuring 76.2 cm (30 in) in diameter and equipped with an ion gauge and trapped diffusion pump. Throughout the experiment, a vacuum of 670 μ Pa to 1870 μ Pa, gauge (2×10^{-7} in to 5.5×10^{-7} in Hg, gauge) was maintained. Three independent and prepositioned thermocouples monitored the chamber temperature at all times.

2.6 TESTING

Tensile tests of the "Kapton" adherends and lap shear tests of adhesively bonded "Kapton" films were performed on an Instron Universal Testing Instrument Model TT-6 according to ASTM Designation D882-61T. Specimens were tested at a cross-head speed of 0.51 cm (0.2 in.)/min. using a gauge length of 7.62 cm (3 in.). Elevated temperature testing at 575K was conducted in an Instron Environmental Chamber wherein each specimen was soaked for 10 min. at temperature before testing.

3. RESULTS AND DISCUSSION

3.1 RESIN PROPERTIES

The polyimide resins used in this investigation and some of their properties are listed in Table I. The LARC resins, made by reacting DABP with the appropriate dianhydride monomers in diglyme at 15% solids (w/w), yielded high molecular weight polyamic acids as indicated by the inherent viscosities (η_{inh}). Films cast from the LARC amic acid solutions and cured at 573K were clear

yellow and flexible. Glass transition temperatures of the polyimide films as determined by DSC ranged from 520K (477°F) for LARC-2 to 570K (567°F) for LARC-4. A film made from the monomeric NMP/ethanol solution of NR-150-B2X and cured to 573K, was clear purple in color and brittle, but self-supporting. The T_g of this material was found to be 595K (612°F) by DSC, compared to 596K (613°F) reported by DuPont⁽⁵⁾.

Dynamic TGA curves of the polyimide films cured at 573K in air are presented in Figure 2. LARC-2 and LARC-3, which possessed the lower T_g values were the most thermally stable when heated in a nitrogen atmosphere. Isothermal TGA curves of LARC-3 and NR-150-B2X aged at 575K in nitrogen are shown in Figure 3. Both adhesives displayed excellent thermal stability with losses of 4.5% for LARC-3 and only 3.2% for NR-150-B2X after 500 hours at 575K.

3.2 BONDING CONDITIONS

The procedure developed for bonding thin "Kapton" film using any of the LARC adhesives or NR-150-B2X has demonstrated excellent feasibility for large-scale bonding. "Kapton" film as thick as 0.127 mm (5 mil) was bonded in 20 seconds at 616K (650°F) with only contact pressure of a small iron used as a heat source. The 0.64 cm (1/4 in.) overlap of the "Kapton" bondlines allowed an easy escape for any volatiles and yielded bondlines that were relatively

void-free. In addition, there was little or no adhesive flash evolved during the bonding of the LARC or NR-150-B2X materials, which indicated that the B-stage prior to bonding allowed adequate, but not an excessive amount of flow. The overall bonding procedure was facile and economical, both of which are desirable attributes for bonding thin film for future large space structures.

In particular, the LARC adhesive materials proved advantageous because the non-toxic diglyme used as a solvent for these adhesives was readily removed during the bonding procedure. An additional advantage exhibited by the LARC resins was that LARC-2, LARC-3, and LARC-4 formed clear, flexible self-supporting films when cast from diglyme in the polyamic acid form and B-staged to 448K (347°F). Therefore these materials could be supplied in the form of a film tape, which would eliminate working with a solvent and facilitate bonding.

3.3 "KAPTON"/"KAPTON" BONDING STRENGTHS

Results from the room temperature and elevated temperature lap shear tests of LARC-2, LARC-3, LARC-4, and NR-150-B2X "Kapton"/"Kapton" bonds are shown in Figure 4. Each data point represents the average lap shear strength of eight individual specimens. Average deviations from the mean values ranged from 68 kPa (10 psi) at RT and 41 kPa (6 psi) at

elevated temperatures for the LARC adhesive specimens to 96 kPa (14 psi) at RT and 37 kPa (5.4 psi) at elevated temperatures for the NR-150-B2X specimens. The average deviation for NR-150-B2X lap shear specimens at 575K was 61% less than the deviation at RT. Failure in all cases occurred in the adhesive. Percent retention of room temperature lap shear strengths at elevated temperature were as follows:

- (1) 27% at 575K (575°F) and 28% at 589K (600°F) for LARC-2 specimens
- (2) 33% at 575K (575°F) and 21% at 589K (600°F) for LARC-3 specimens
- (3) 49% at 575K (575°F) and 53% at 589K (600°F) for LARC-4 specimens
- (4) 56% at 575K (575°F) for NR-150-B2X specimens.

At 575K, the materials possessing the higher T_g values retained RT properties better than those with the lower T_g values (Table I). LARC-4 and NR-150-B2X possessing the higher T_g values in the range of the test temperature displayed the greatest retention in strength.

The effect of adherend thickness on lap shear strength is presented in Figure 5 for LARC-3 "Kapton"/"Kapton" bonds. RT strength was found to be dependent upon the thickness of the adherends. Failure for all bonds occurred in the adhesive except for those specimens bonded with the thinner 0.025 mm (1 mil) "Kapton" adherends. Failures for the 0.025 mm

"Kapton" specimens were 50% adhesive and 50% failure in the adherend itself (see Figure 1). For these particular thin film joints, the adhesive was as strong as or in some cases stronger than the film to which it was bonded.

3.4 THERMAL AGING IN VACUUM

Isothermal aging of lap shear specimens comprised of LARC and NR-150-B2X adhesives bonded to 0.051 mm (2 mil) "Kapton" was performed in vacuum at 575K. After aging between 500 and 1000 hours, a darkening in color of the bondlines and of the adherends themselves was observed. Room temperature lap shear strengths of the bondlines obtained after 0, 250, 500, 1000, 1500, 2000, and 3000 hours aging are shown in Figure 6. RT strengths of all of the adhesives peaked at 500 hours, indicative of a postcuring effect. A second rise in strength which was most prominent for LARC-2 and LARC-3 occurred around 1500 hours. After 3000 hours aging, the RT strengths of all four adhesives were still increasing, probably due to a gradual crosslinking of the polymer systems. Figure 7 shows the lap shear data for the specimens aged at 575K in vacuum and tested at 575K. All adhesives tested at elevated temperature increased in strength while aging for the first 1000 hours. After 1500 hours, the strength of NR-150-B2X leveled at approximately 620 kPa (90 psi) which was the highest lap shear strength obtained

for any of the adhesives tested at elevated temperature. This high strength was probably due to the higher T_g of this material. The strength of LARC-4 specimens, however, changed the least from 0 to 3000 hours aging and was rising at the end of 3000 hours. Table III exhibits the percent retention of room temperature properties for all adhesive specimens tested at 575K. At elevated temperature, LARC-4 and NR-150-B2X retained about 50% of their original RT lap shear strengths.

Thermomechanical analysis (TMA) was used to measure the T_g values of the actual adhesive "Kapton"/"Kapton" bondlines before and after aging in vacuum at 575K. Figure 8 shows a plot of T_g versus time where each symbol represents an average of four data points. After aging for 500 hours all adhesives had reached their ultimate T_g compared to those determined previously for the fully cured polymers by DSC (Table I). After aging 3000 hours, T_g values of NR-150-B2X and LARC-4 remained constant, but those values obtained for LARC-2 and LARC-3 were still increasing. TMA curves obtained from 1 cm x 1 cm samples cut from the adhesive bonds are presented in Figure 9. The LARC-3 curves, which are representative of the LARC adhesive series, showed an increase in T_g from 520K (477°F) to 571K (568°F) on aging 3000 hours, but no significant change in the amount of probe dis-

TABLE III. PERCENT OF RT STRENGTH BEFORE AND AFTER AGING AND TESTING AT 575K IN VACUUM

Adhesive	at 0 hrs.	after 1000 hrs.	after 2000 hrs.	after 3000 hrs.
LARC-2	27%	46%	41%	42%
LARC-3	33%	46%	41%	37%
LARC-4	49%	52%	48%	50%
NR-150-B2X	56%	60%	48%	49%

placement $5\mu\text{m}$ (0.19 mil). The T_g of NR-150-B2X specimens also rose from 550K (531°F) at 0 hours to 616K (649°F) after 3000 hours. Unlike the case of LARC-3, the probe displacement for NR-150-B2X bondlines was 96% less after aging [from $51\mu\text{m}$ (2.0 mil) to $2\mu\text{m}$ (0.08 mil)]. Such behavior of the NR-150-B2X curve at 0 hours aging demonstrates the plasticizing of this material due to residual NMP solvent. Upon curing at elevated temperature, the solvent is then removed. The bonding process used for this adhesive was therefore not sufficient for complete solvent removal. This ability of NMP to remain attached to the NR-150 polymers and other polyimides well over its boiling point temperature has been recognized previously. Whether or not the presence of NMP in the NR-150-B2X "Kapton"/"Kapton" bondline is detrimental remains to be concluded.

4. CONCLUSIONS

Four experimental polyimide materials covering a 75K (135°F) range in T_g have been developed as high tem-

perature adhesives for bonding "Kapton" film. A unique bonding process requiring only 20 sec. time at the bonding temperature and minimal pressure was developed which shows promise for the large-scale bonding of thin "Kapton" sheet film for future large space structures. All four of the candidate polyimides show excellent potential as adhesives for "Kapton" bonding. NR-150-B2X and LARC-4, the materials characterized by the higher T_g s, exhibited the best retention of properties on long term aging at elevated temperature in vacuum. The main advantage offered by the LARC adhesives is that these materials can be supplied in the form of a flexible tape already B-staged and ready for instant bonding. In addition, the non-toxic ether solvent diglyme from which the LARC resins were prepared, was easily removed on bonding, disallowing any plasticization of the polymers by solvent, as compared to the NMP problem with NR-150-B2X. The relatively simple bonding process involved coupled with the ease in handling these materials make

the adhesives studied attractive for use in bonding "Kapton" film.

5. ACKNOWLEDGEMENT

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7. BIOGRAPHY

Anne St. Clair received a B.A. degree in Chemistry from Queens College in 1969 and M.S. in Chemistry from Virginia Polytechnic Institute and State University in 1972. From 1972 to September 1977, she was employed as a Research Associate at NASA-Langley Research Center. She recently joined the Polymer Group at NASA-Langley where she serves as an Aerospace Technologist in the field of high temperature polymers.

Wayne Slomp is an Aerospace Materials Engineer at NASA-Langley where he has been employed since 1958. He received his B.S. in Physics (1958) from Emory and Henry College. His field of research has concerned environmental effects on polymeric materials and coatings.

Terry St. Clair received his B.S. degree in Chemistry from Roanoke College in 1965 and his Ph.D. in Organic Chemistry from Virginia Polytechnic Institute and State University in 1972. From 1972 to 1975, he served as a Post-doctoral research associate at NASA-Langley. In 1975, he was employed by NASA-Langley as an Aerospace Technologist where he has been responsible for research and development of high temperature adhesives and composites.

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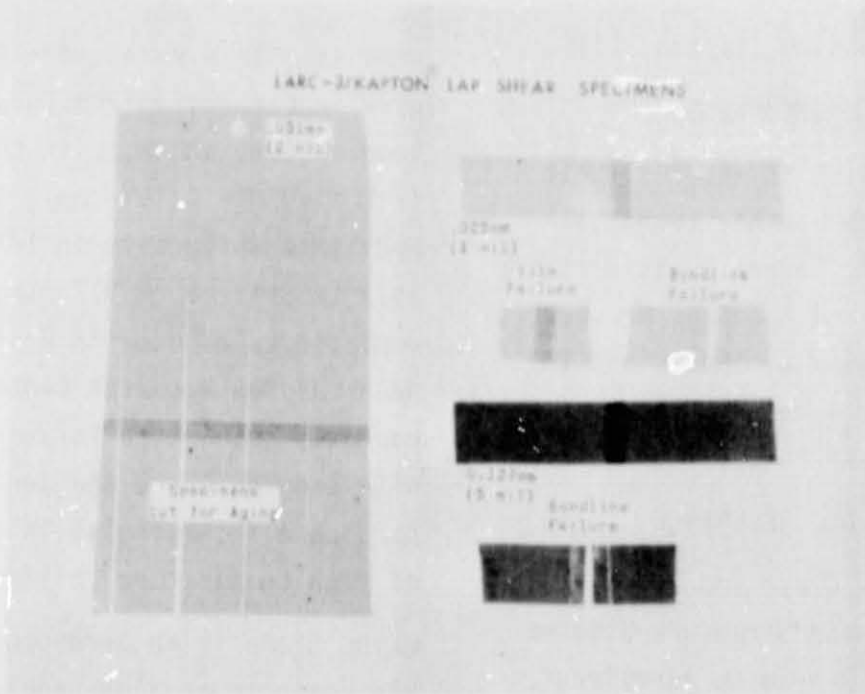


FIGURE 1. LARC-3/ Kapton lap shear specimens before and after testing.

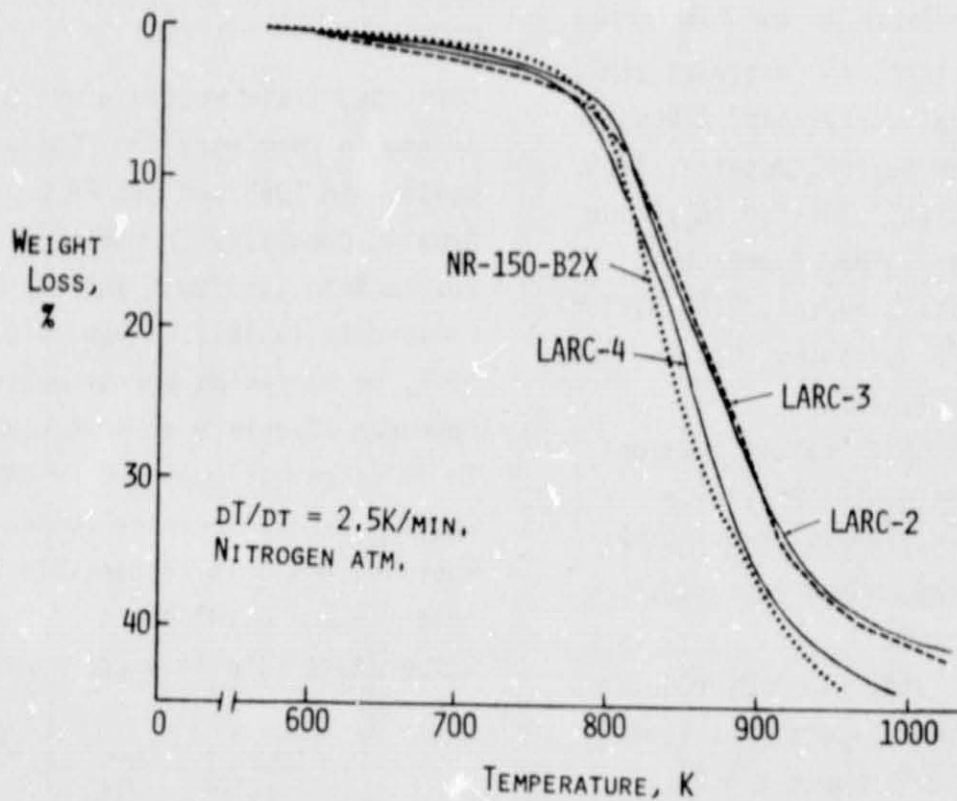


FIGURE 2. Thermograms of polyimide films cured at 573K in air.

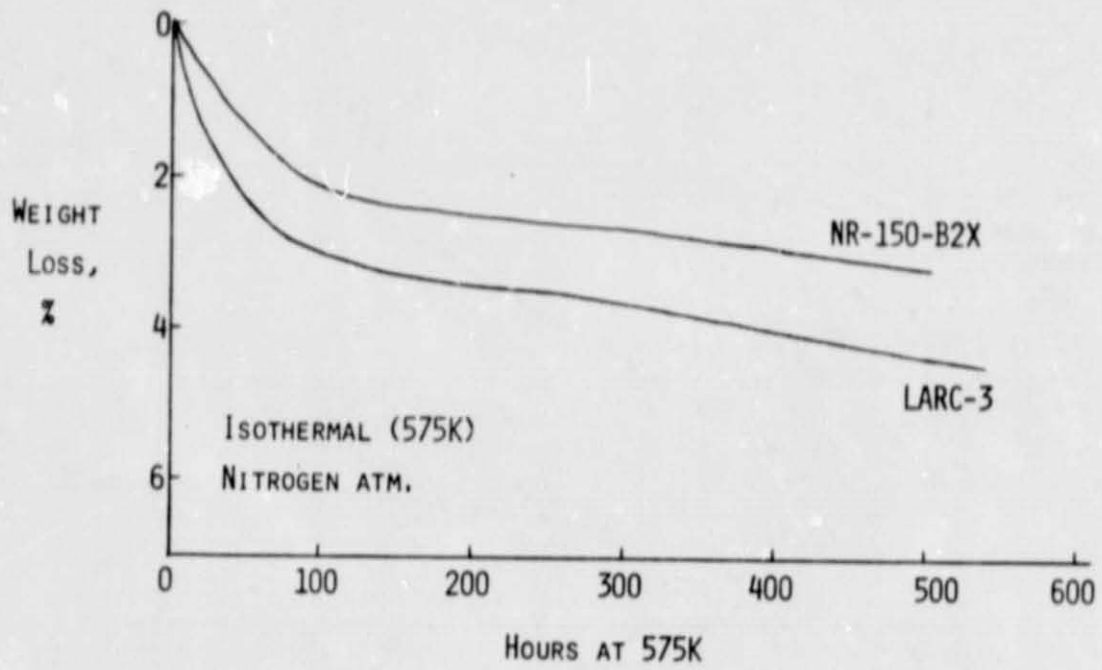


FIGURE 3. Isothermal TGAs of polyimide films cured at 573K in air.

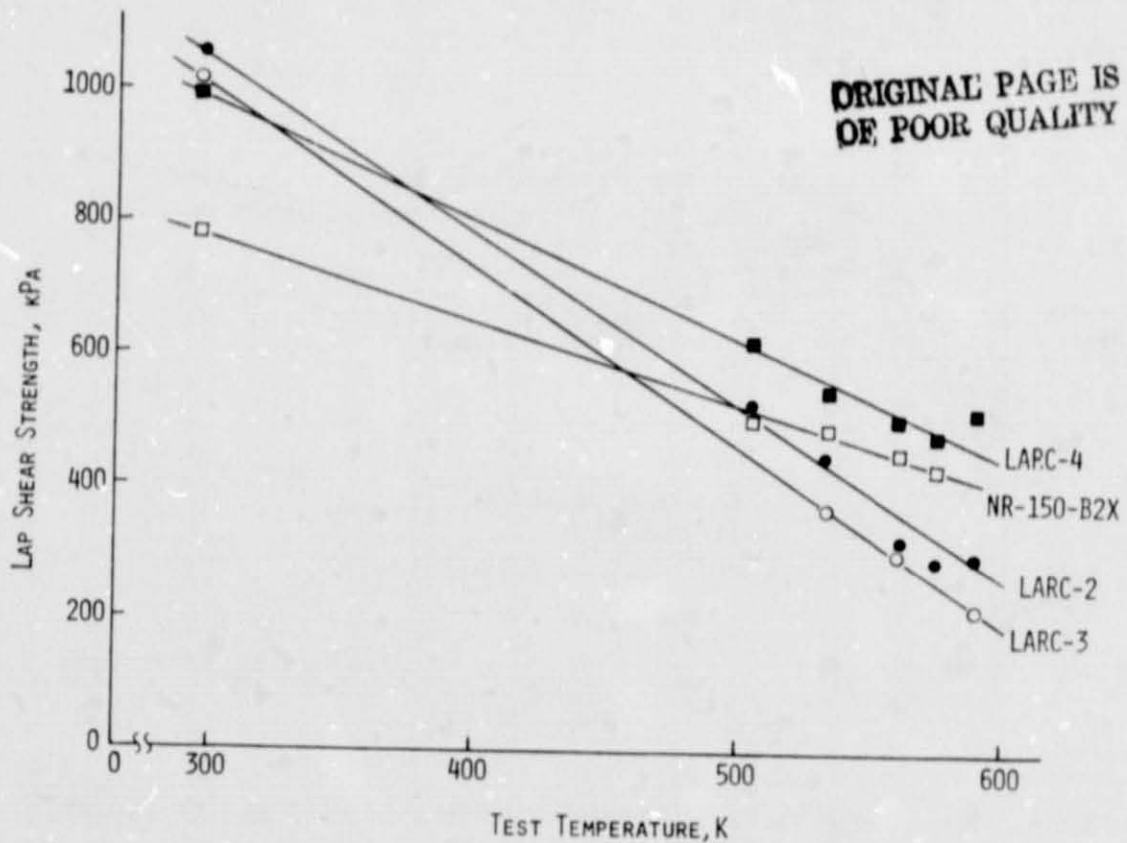


FIGURE 4. Lap shear strengths of LARC adhesives and NR-150-B2X bonded to 0.051 mm (2 mil) Kapton.

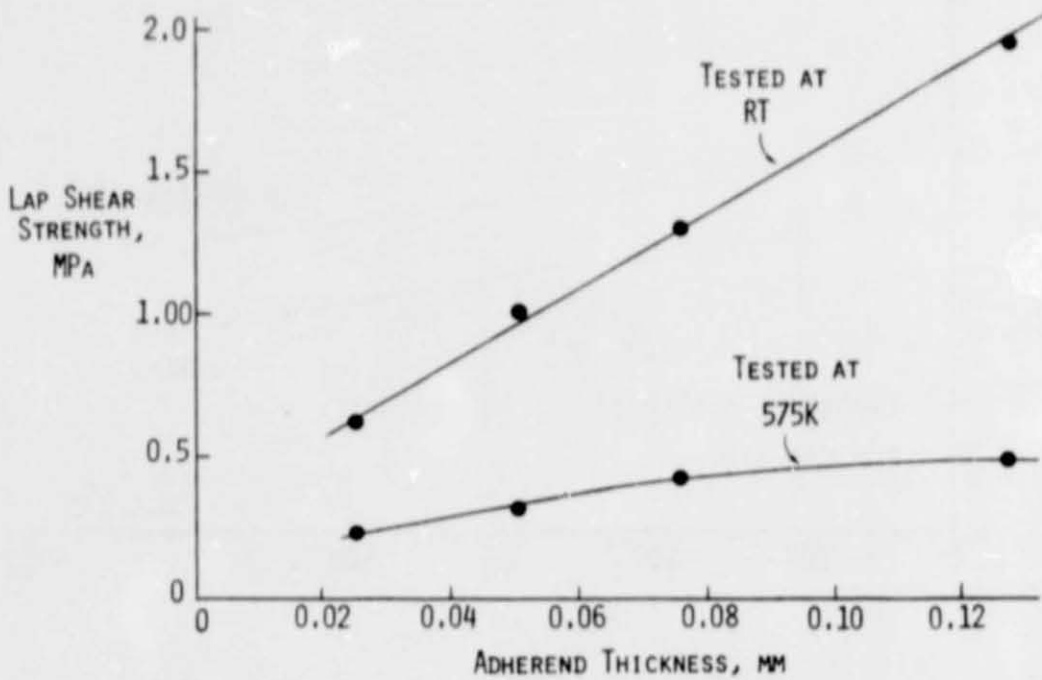


FIGURE 5. Room temperature and elevated temperature lap shear strengths of LARC-3 bonded to varying thicknesses of Kapton.

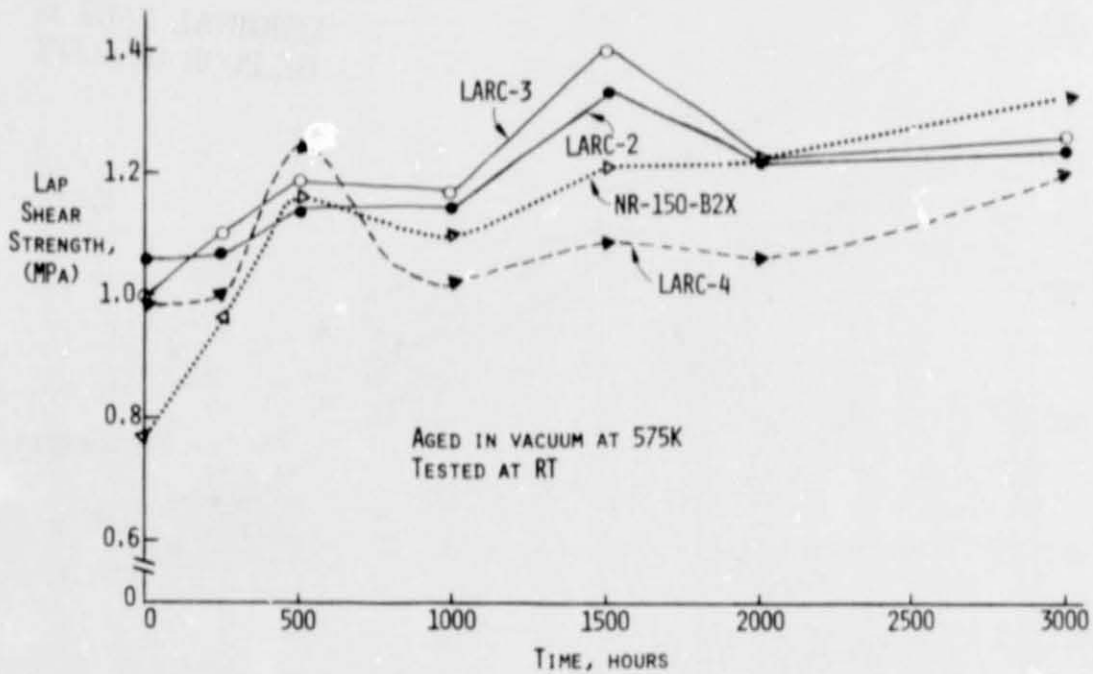


FIGURE 6. Room temperature lap shear strengths of LARC and NR-150-B2X Kapton/Kapton specimens aged in vacuum at 575K.

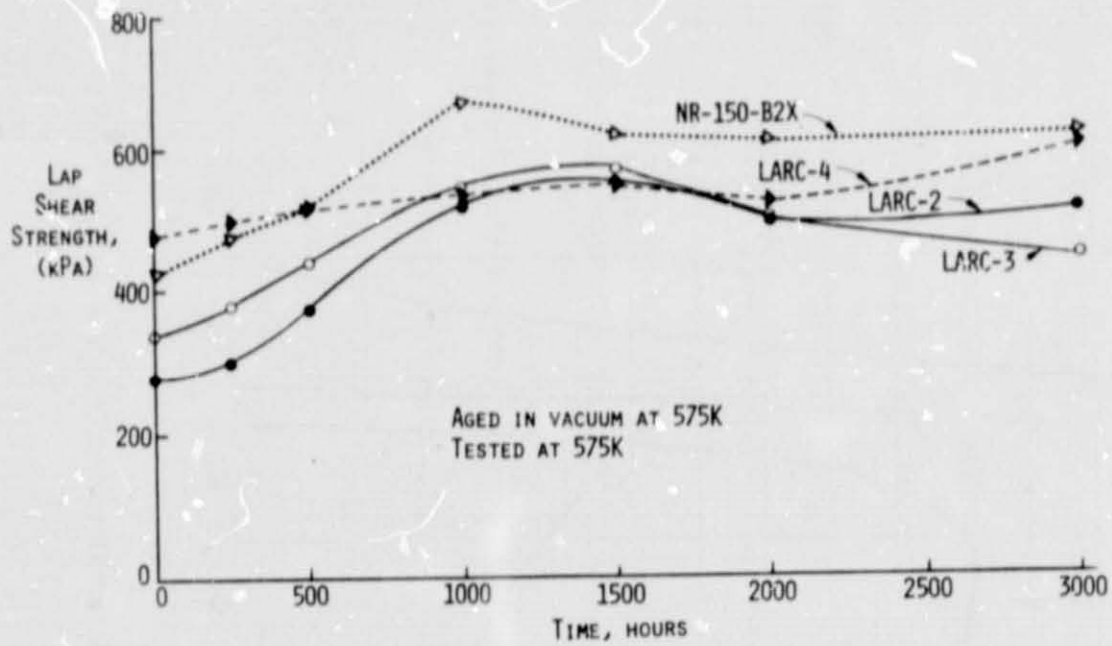


FIGURE 7. Elevated temperature lap shear strengths of LARC and NR-150-B2X Kapton/Kapton specimens aged in vacuum at 575K.

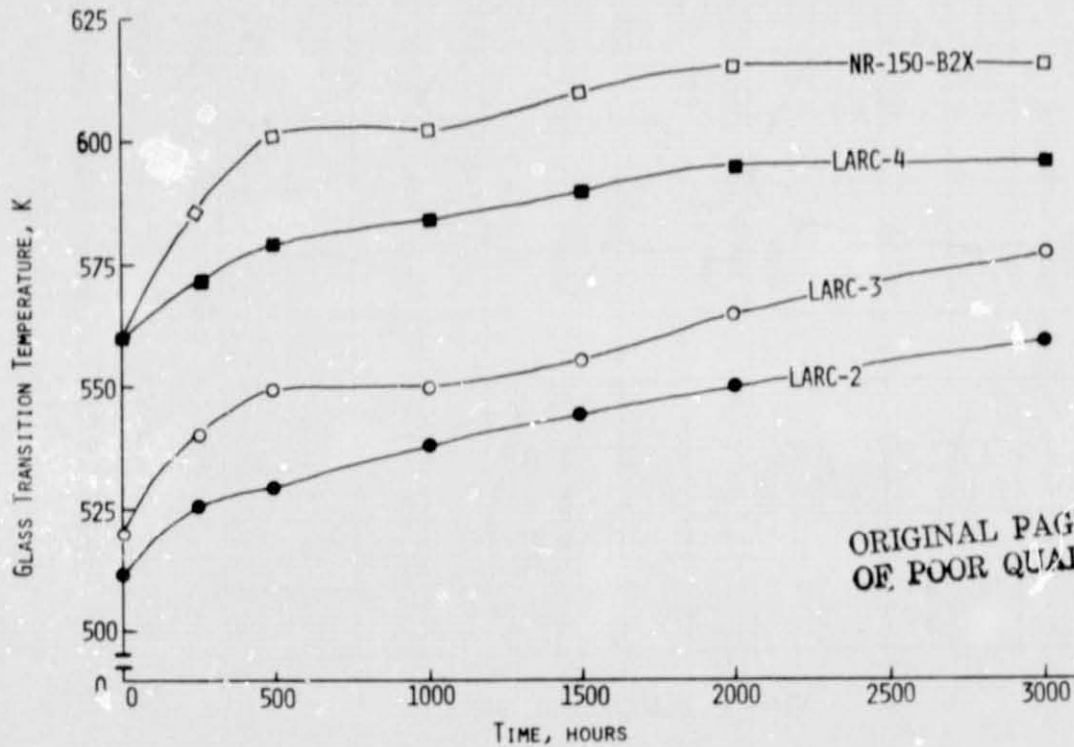


FIGURE 8. T_g s of LARC and NR-150-B2X Kapton/Kapton bondlines after aging in vacuum at 575K.

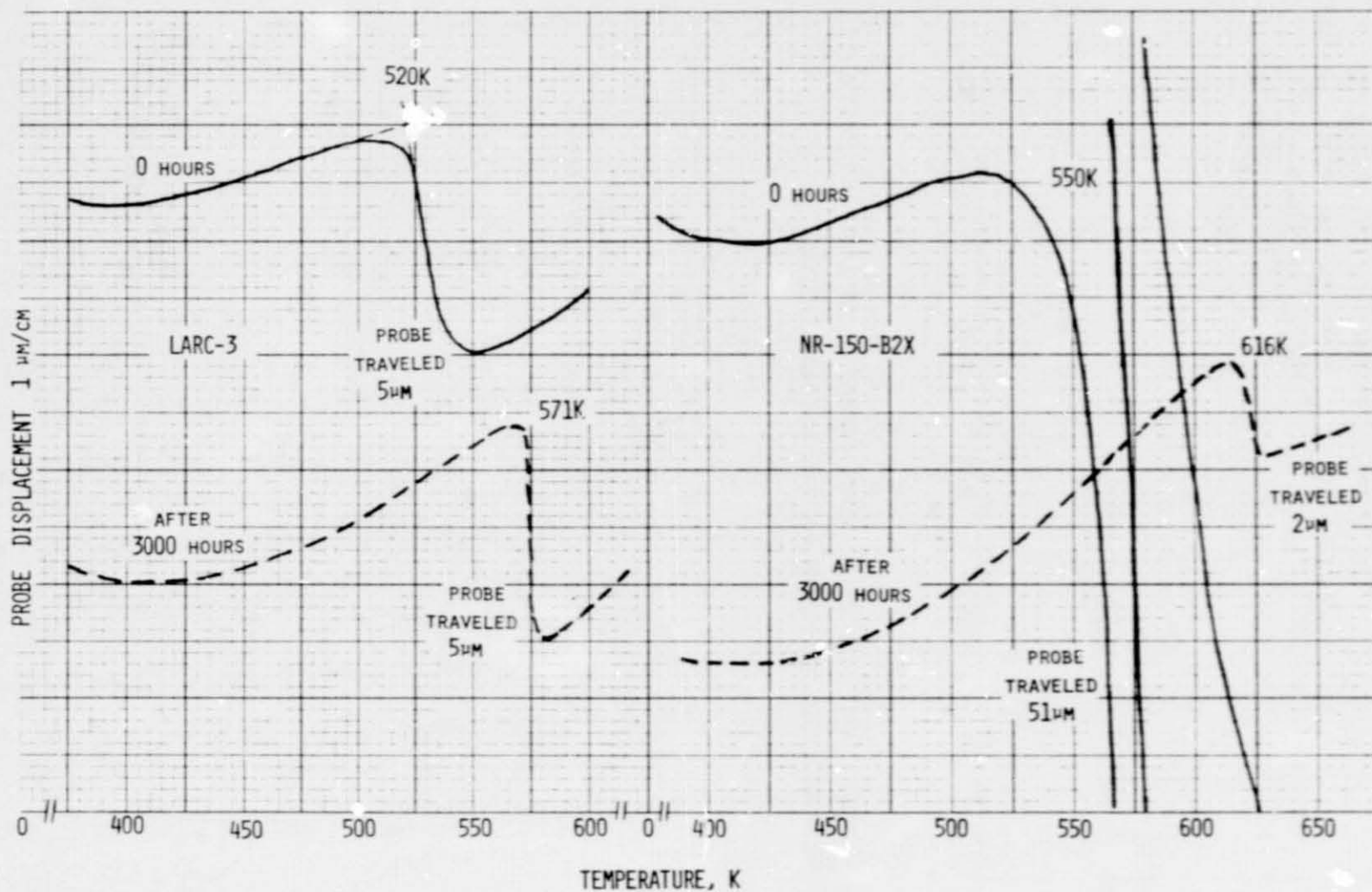


FIGURE 9. TMA curves of LARC-3 and NR-150-B2X Kapton/Kapton bondlines before and after aging 3000 hours in vacuum at 575K.