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NASA Technical Memorandum 104202

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FILMS AFTER EXPOSURE TO HIGH pH**

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(NASA-TM-104202) THE MECHANICAL PROPERTIES
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(NASA) 33 p CSCL 11C

N92-22666

G3/27 Unclass
0081278

JANUARY 1992



National Aeronautics and
Space Administration

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The Mechanical Properties of Polyimide Films After Exposure to High pH

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INTRODUCTION

Polyimide insulated electrical wire has been used in the aerospace industry in commercial, military, and to a lesser degree, general aviation aircraft since the early 1970's. The insulation offers benefits in terms of compact physical size, its ability to maintain good mechanical strength at high temperature, and good dielectric strength.

Polyimide insulated wire is routinely exposed to high humidity, alkaline cleaners, and paint removers while under mechanical stresses due to the nature of the wiring and its installation in aircraft. Electrical insulating materials are known to deteriorate by a number of chemical and physical mechanisms which can be related to the polymer structure and the intensity of the various service stresses acting upon it. A predominate mechanism of deterioration is believed to be hydrolysis, a chemical reaction of water or aqueous fluids with the polymer chain. Hydrolytic chain-scission reduces the average chain length resulting in loss of strength and other properties. The rate of hydrolysis has been shown to be dependent upon the mechanical stresses from bending and stretching[1-2].

Many polyimides exhibit excellent chemical resistance and do not deteriorate by certain chemical and physical mechanisms. The purpose of this paper is to summarize the mechanical properties of fourteen commercial and experimental polyimides before and after exposure to high pH solutions in stressed and unstressed configurations. Other material properties investigated include viscosity, glass transition temperature(Tg), dielectric constant, thermogravimetric analysis(TGA), thermomechanical analysis(TMA), and moisture absorption.

*Lockheed Engineering and Sciences Company

EXPERIMENTAL

Commercially available films* used in this study are listed below.

Material	Manufacturer
KAPTON® 200HN	DuPont, Centerville, OH
UPILEX®R	UBE Industries, LTD, Japan
UPILEX®S	UBE Industries, LTD, Japan
APICAL® 300AV	Allied Signal, Des Plaines, IL
LaRC™-TPI	Mitsui Toatsu Chemicals, Tokyo, Japan

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

POLYMER SYNTHESIS

The polyamide acids were prepared at a concentration of 20% solids (w/w) by the slow addition of a stoichiometric amount of the dianhydride in powder form to a magnetically stirred solution of the diamine in N,N-dimethylacetamide (DMAc) under a nitrogen atmosphere at room temperature (RT). Polymerization solutions were stirred overnight and inherent viscosities (η_{inh}) at 0.5% concentration in DMAc were subsequently determined at 35°C.

The dianhydrides and diamines used to make the experimental films for the study follow.

Material	Acronym	Source	Purification
4,4'-Isophthaloyl diphthalic anhydride	IDPA	NASA-LaRC[3]	Vacuum dried at 125°C
4,4'-Oxydiphthalic anhydride	ODPA	Occidental Chemical Corporation	Sublimed at 200-210°C
Hydroquinone diether anhydride	HQDEA	Occidental Chemical Corporation	Used as received
2,2-Bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride	6F	Hoechst Celanese	Used as received
Pyromellitic dianhydride	PMDA	Allco Chemical Corporation	Used as received
3,3',4,4'-Benzophenone tetracarboxylic dianhydride	BTDA	Allco Chemical Corporation	Sublimed at 200-210°C
3,3',4,4'-Biphenyl tetracarboxylic dianhydride	BPDA	Mitsubishi International Corp.	Used as received
1,3-Phenylenediamine	m-PDA	Fluka AG	Used as received
1,4-Phenylenediamine	p-PDA	Fluka AG	Recrystallized from ethanol and sublimed at 120°C
3,4'-Oxydianiline	3,4'-ODA	Kennedy and Klim, Inc.	Used as received
4,4'-Oxydianiline	4,4'-ODA	Kennedy and Klim, Inc.	Used as received
3,5-Diaminobenzotrifluoride	DABTF	Occidental Chemical Corporation and NASA-LaRC[4]	Used as received
2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane	BDAF	Central Glass Company, LTD	Recrystallized from dichloromethane and hexane
1,3-Bis(4-aminophenoxy-4'-benzoyl)benzene	BABB	DayChem Laboratories, Inc.	Recrystallized from toluene

FILMS

The polyamide acid solutions were centrifuged, the decantate cast onto plate glass using a 23 mil doctor blade, and allowed to dry to a tack-free form in a dust-free chamber at RT, continually purged with dry air. The films on glass were then thermally converted to the polyimide by heating in a forced air oven at 100, 200, and 350°C for 1 h at each temperature. LaRC™-CPI was heated to 300°C. Cooled films were removed from the glass plates by immersion in warm water. Mechanical properties of the 2.0-2.5 mil thick films were determined as recommended in ASTM D882 using a minimum of five specimens per test condition.

CHARACTERIZATION

Inherent viscosities were measured in 0.5% solution (w/v) in DMAc at 35°C. Glass transition temperatures (T_g), determined by Differential Scanning Calorimetry (DSC) were performed on a DuPont 990 Thermal Analyzer in conjunction with a Model 910 Differential Scanning Calorimeter at a heating rate of 20°C/min. Polyimides were heated to ~ 100°C above the T_g , quenched, and rerun to obtain the T_g . The T_g s were obtained from the second heating at the midpoint of the ΔT versus temperature curve. Dielectric constants were obtained from various sources including literature values. Direct comparisons should not be made since the instruments and methods by which the values were determined were not consistent for each polyimide. Dynamic TGA was performed on a Seiko Model TG/DTA 220 at a heating rate of 2.5°C/min and an air flow of 15cc/min. Samples were held at 100°C for 30 min and then heated to 650°C. Temperature at which 5% weight loss occurred was reported. T_g s were also determined by TMA on a DuPont 9900 Computer Thermal Analyzer. Samples were heated to 400°C at a heating rate of 5°C/min. Moisture absorption was determined by weighing a clean 3 x 5 in piece of film and placing it in a drying oven overnight at 100°C. The film was removed, reweighed, and submersed in water for 31 days. After immersion, the film was blotted dry and weighed again. Moisture regain was determined by the amount of weight gained.

TENSILE PROPERTIES OF THIN FILMS

A Model 2000/2 table-top SINTECH load frame, equipped with a CompuA₂ Model 286 computer and HP graphics plotter, was used for measuring tensile properties. Pneumatically actuated, one inch grips with steel faces were used for clamping the polyimide films. All mechanical property measurements were performed at RT.

The tensile specimens were 0.200 in wide and varied in length from 4-6 inches. At least 2 in beyond the gauge length was required for clamping purposes. Each specimen thickness was determined to within 0.0001 in with Testing Machines, Inc. Models 549M and 49-70 electronic micrometers. Thickness measurements were made at every inch over the specimen length and the average was used for the calculations. Film thickness for experimental films was approximately 2.0-2.5 mil and commercial films of the same thickness were obtained where available. Film strips were initially cut to 0.200 in width using a machined device that held a series of razor blades at 0.200 in intervals and was pulled on top of guide rests over the polyimide film. Later in the study, films were cut more accurately with a 0.200 in Thwing-Albert JDC Precision Cutter. A minimum of five samples were used for each condition. A crosshead speed of 0.200 in/min was used for determination of elastic modulus, tensile strength and elongation at break.

A baseline for unexposed films was established for each of the three configurations shown in Figures 1 and 2. Normal(unstressed) configurations were placed in solvents, flat and horizontal to each other. Rolled configurations were wrapped around a 0.25 in diameter tube and secured by a polyethylene paper clip. Twisted configurations were clamped in a machined stainless steel device with four twists per specimen over a length of four inches.

The tensile specimens used in this study were smaller in size than recommended in ASTM Standard D882, but this standard was used as a guide. The ratio of length to width was 10:1. A data base using 0.200 in width of KAPTON® and ULTEM® compared to full sizes(1 x 10 in) clearly indicated that for measurements of changes in tensile properties, data obtained for smaller specimens was acceptable[5].

Films were immersed for 48 h at RT in the following basic solutions: 1M ammonium hydroxide (7% v/v, pH = 11), 1M sodium carbonate (11% w/v, pH = 12), 0.5M trisodium phosphate (19% w/v, pH = 13) and 1M sodium hydroxide (4% w/v, pH = 14). After exposure, the specimens were removed, washed with tap water and rinsed with distilled water. They were blotted dry and placed in a desiccator.

RESULTS AND DISCUSSION

Table I lists the inherent viscosities of the various polyamide acids, Tgs of the imidized films by DSC and the dielectric constants. Inherent viscosities for the polyamide acid solutions ranged from 0.48 dL/g to 1.79 dL/g. Films of the polyimides varied in color from nearly transparent to light orange-brown after heating to 350°C, where all films should be fully imidized. All films were clear except LaRC™-CPI, which

was translucent and exhibited some degree of crystallinity. Most of the polyimides were amorphous with T_{gs} from 222°C to greater than 500°C. LaRC™-CPI and ODPA/p-PDA were semi-crystalline as evidenced by X-ray diffraction. Polyimides are used widely in electronic applications because they have low dielectric constants. Variations in the backbone structure, such as the introduction of fluorine atoms, tend to afford better insulative properties, substantially improve thermo-oxidative stability, minimize moisture pick-up and lower chain-chain interactions[6]. The dielectric constant of the state-of-the-art polyimide presently used for advanced electronics applications generally ranges from 3.2-4.0 depending on measurement frequency and moisture content of the polyimide. Two systems that exhibited dielectric constants below 2.6 were 6F/3,5-DABTF and HQDEA/4-BDAF[4,7]. Table II lists TGA data with 5% weight loss ranging from 480 to 583°C. Several systems that showed low moisture regain of approximately 1% or less included LaRC™-CPI, LaRC™-TPI, UPILEX®R, 6F/3,5-DABTF, and HQDEA/4-BDAF as shown in Figure 3. Crystallinity or contiguity may contribute to low moisture absorption in LaRC™-CPI and UPILEX®R while the 6F/3,5-DABTF and HQDEA/4-BDAF systems contained fluorine atoms in the backbone which tend to impart low moisture pick-up. The tendency for polyimides to absorb moisture impacts their electrical performance and processability[8]. Many PMDA/ODA polyimides, including KAPTON® and APICAL®, exhibited high moisture absorption.

The polyimides in this evaluation were subjected to basic solutions, pH 11-14, and their retention of mechanical properties, tensile strength, tensile modulus, and elongation at break, were determined. The chemical structure of the diamine and dianhydride, strength of the imide links, incomplete imidization after curing, morphology, and water absorption are several factors that can affect hydrolysis(J. A. Kreuz, DuPont).

Nominal changes in thickness before and after exposure were recorded to identify those polyimides that swelled during exposure. The PMDA/4,4'-ODA and ODPA/p-PDA systems swelled as much as 56% and 40% respectively in sodium hydroxide with smaller increases in the less basic solutions. Other systems showed only a small increase.

Caustic solutions were selected because they accelerated hydrolysis, were found in cleaning solutions used in aircraft maintenance, and they provided a range of pH values. Three configurations were chosen to simulate unstressed and stressed conditions for the film specimens. The normal configuration was unstressed, and was used as a baseline to evaluate any affects induced by the other conditions. The rolled configuration induced a maximum stress of approximately 4 ksi, using a nominal 500 ksi modulus, 0.200 in width and 2 mil thickness in the approximation. The twisted configuration induced approximately 2.3 ksi, based on uniform twist in the specimens.

Figures 4 and 5 compare the three configurations for KAPTON®200HN and APICAL®300AV film. APICAL® is believed to be the same chemical structure as DuPont's KAPTON®. Both systems exhibited similar degradation in the ammonium hydroxide and sodium hydroxide solutions. Specimens tore from the stress induced by the twisting in the trisodium phosphate exposure and mechanical data could not be determined. Modulus and elongation were essentially unaffected by the exposure in the basic solutions in most cases. KAPTON® and APICAL® retained approximately 100% of modulus except in cases of complete degradation as shown in Tables III and IV. Modulus is dependent on the intermolecular forces whereas tensile strength depends strongly on molecular weight and would be affected when chain length is reduced. Elongation is dependent on film quality and therefore, no direct correlation can be drawn. Elongation greatly decreased in the ammonium hydroxide and trisodium phosphate solutions. Degradation is connected with the hydrolysis of the imide moiety. Resistance to hydrolysis seems to depend strongly on the chemical nature of the dianhydride component of the polymer. PMDA based polyimides appear to be the least resistant to hydrolysis of the polyimides studied[9].

Figure 6 shows the tensile strength of UPILEX®R. In the rolled configuration, there is a significant drop in tensile strength during exposure with only 65% retention. Since UPILEX®R is a commercially available film, it is possible that the surface of the film differs from the interior portions. In that configuration, the stress is greater on the surface and the surface becomes more susceptible to attack and degradation. The elongation dropped in the rolled configuration, similar to the decrease observed in the tensile strength for the same configuration, as shown in Table V. It can be seen from Figure 7 that UPILEX®S exhibited similar behavior as the UPILEX®R, having a reduction in tensile strength of 30% in the rolled configuration but being unaffected in the twisted configuration except in the sodium hydroxide solution. Modulus and elongation were not greatly affected except in the sodium hydroxide solution as shown in Table VI.

Figure 8 compares LaRC™-TPI data, which shows no drastic reduction induced by solvent or stress. Table VII shows the effects of exposure on modulus and elongation. LaRC™-CPI(unoriented) maintained excellent retention of tensile strength in all cases(Figure 9). Modulus and elongation were not affected by the stress or hydrolysis(Table VIII). LaRC™-ITPI exhibited good retention of tensile strength as shown in Figure 10. The increase in tensile strength in the rolled and twisted configurations is attributed to better monomer purity in the synthesis of the polymer. Good retention of modulus and elongation were maintained, as shown in Table IX.

Figure 11 and Table X compare tensile strengths, elongations and moduli of HQDEA/4-BDAF. It exhibited excellent retention of tensile strength, modulus and

elongation in almost all cases. Another fluorinated polymer evaluated is shown in Figure 12. The BPDA/3,5-DABTF performed well except in the most caustic solution under stress. The twisted specimens in the sodium hydroxide test were deformed from curling and mechanical data could not be obtained. Table XI compares retention of mechanical properties after exposure. Retention of modulus was excellent for all configurations. Elongation was affected in ammonium hydroxide and sodium hydroxide solutions. However, since the elongation is strongly dependent on film quality and edge effects, it is difficult to draw a direct correlation to the exposure conditions. Figure 13 shows excellent retention of tensile strength in the normal and rolled configurations of the 6F/3,5-DABTF system. However, the twisted configuration shows the film specimens broke at the twisted sections during the exposure in ammonium hydroxide, trisodium phosphate and sodium hydroxide. The film was brittle and therefore will be most affected by the stress induced from twisting. These stress sites would be more susceptible to attack from the more caustic solutions. Modulus retention was excellent and elongation retention was good, as shown in Table XII.

Figure 14 showed that ODPA/p-PDA exhibited good retention of tensile strength for the normal and rolled configurations, but specimens broke from the twisting stress prior to exposure in the basic solutions. Modulus and elongation retention were good, as shown in Table XIII. Figure 15 and Table XIV compare the ODPA/3,4'-ODA system, which generally exhibited excellent retention of tensile strength, modulus and elongation. Figure 16 compares two PMDA based systems for the normal configuration only. PMDA/3,4'-ODA did not perform well in the exposure and was not evaluated in the stressed configurations. The laboratory version of KAPTON® (PMDA/4,4'-ODA) was only evaluated in the normal configuration. ODPA based polyimides were more resistant to base hydrolysis than similar PMDA polymers.

SUMMARY

In this study, several polyimides were selected for evaluation for resistance to degradation to various aqueous solutions. Commercially available PMDA based films appeared to be the least resistant to hydrolysis of the polyimides evaluated. UPILEX® films showed good retention of properties except in the rolled configuration, where they showed a significant loss in tensile strength. LaRC™-TPI exhibited good retention also. Of the experimental films synthesized, LaRC™-CPI, ODPA/3,4'-ODA, and HQDEA/4-BDAF exhibited excellent resistance to base hydrolysis while under stress. Modulus and elongation were generally not greatly affected by the exposure to the basic solutions.

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Table I - Physical Properties of Polyimides

Polyimide Film	Polyamide acid Inherent Viscosity, dL/g	Tg, °C	Dielectric Constant
LaRC-ITPI	0.51, 0.47	259	3.29*
LaRC-CPI	1.38, 1.57	222 (Tm = 350)	3.10
LaRC-TPI (comm.)	—	250	3.30
6F/3,5-DABTF	0.58, 0.48	297	2.58
BPDA/3,5-DABTF	0.96, 0.77	329	3.02
HQDEA/4-BDAF	0.68, 0.57	227	2.56
ODPA/3,4'-ODA	1.60, 1.79	245	3.06
PMDA/3,4'-ODA	0.70	>325	3.18
ODPA/p-PDA	0.81	none (crystalline)	—
PMDA/4,4'-ODA	0.86	297	—
KAPTON®	—	(400)	3.20
APICAL®	—	(400)	3.00
UPILEX® R	—	285	3.50
UPILEX® S	—	>500	3.50

* Calculated value of dielectric constant provided by J. R. Pratt, Amoco, Atlanta, GA.

Table II - Thermal Analysis Data of Polyimide Films

Polyimide Film	Tg, °C ^a	Tg, °C ^b	TGA, °C ^c
LaRC-ITPI	259	274	481
LaRC-CPI	222 (Tm = 350)	ND ^d	487
LaRC-TPI (comm.)	250	256	532
6F / 3,5-DABTF	297	299	480
BPDA / 3,5-DABTF	329	373	513
HQDEA / 4-BDAF	227	231	490
ODPA / 3,4'-ODA	245	252	497
PMDA / 3,4'-ODA	>325	ND	503
ODPA / p-PDA	ND	ND	515
PMDA / 4,4'-ODA	297	251	495
KAPTON®	ND	ND	528
APICAL®	ND	ND	528
UPILEX® R	285	ND	544
UPILEX® S	ND	ND	583

^a By DSC.

^b By TMA.

^c 5% weight loss.

^d ND = nondetectable.

**Table III - % Retention of Mechanical Properties of KAPTON® 200HN
After Exposure to High pH Solutions**

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal	1M NH ₄ OH	61	100	13
	1M Na ₂ CO ₃	98	100	90
	0.5M Na ₃ PO ₄ •12H ₂ O	61	100	16
	1M NaOH	Degraded	Degraded	Degraded
Rolled	Unexposed	100	100	97
	1M NH ₄ OH	56	100	11
	1M Na ₂ CO ₃	100	100	100
	0.5M Na ₃ PO ₄ •12H ₂ O	79	100	23
	1M NaOH	Degraded	Degraded	Degraded
Twisted	Unexposed	100	99	100
	1M NH ₄ OH	41	100	9
	1M Na ₂ CO ₃	95	97	100
	0.5M Na ₃ PO ₄ •12H ₂ O	*	*	*
	1M NaOH	Degraded	Degraded	Degraded

* Samples tore at twisted section during exposure.

Table IV - % Retention of Mechanical Properties of APICAL® 300AV After Exposure to High pH Solutions

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal	1M NH ₄ OH	50	100	6
	1M Na ₂ CO ₃	90	100	83
	0.5M Na ₃ PO ₄ ·12H ₂ O	52	100	10
	1M NaOH	Degraded	Degraded	Degraded
Rolled	Unexposed	100	100	100
	1M NH ₄ OH	48	100	5
	1M Na ₂ CO ₃	94	99	91
	0.5M Na ₃ PO ₄ ·12H ₂ O	56	100	16
Twisted	1M NaOH	Degraded	Degraded	Degraded
	Unexposed	91	88	100
	1M NH ₄ OH	67	100	7
	1M Na ₂ CO ₃	100	100	68
	0.5M Na ₃ PO ₄ ·12H ₂ O	*	*	*
	1M NaOH	Degraded	Degraded	Degraded

* Samples tore at twisted section during exposure.

Table V - % Retention of Mechanical Properties of UPILEX® R After Exposure to High pH Solutions

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal	1M NH ₄ OH	100	96	100
	1M Na ₂ CO ₃	100	89	100
	0.5M Na ₃ PO ₄ •12H ₂ O	88	91	97
	1M NaOH	72	96	73
Rolled	Unexposed	100	100	100
	1M NH ₄ OH	66	100	57
	1M Na ₂ CO ₃	64	96	59
	0.5M Na ₃ PO ₄ •12H ₂ O	64	96	58
	1M NaOH	67	100	60
Twisted	Unexposed	100	100	100
	1M NH ₄ OH	99	87	100
	1M Na ₂ CO ₃	100	92	100
	0.5M Na ₃ PO ₄ •12H ₂ O	100	99	100
	1M NaOH	73	89	72

Table VI - % Retention of Mechanical Properties of UPILEX[®]S After Exposure to High pH Solutions

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal	1M NH ₄ OH	83	84	100
	1M Na ₂ CO ₃	81	82	100
	0.5M Na ₃ PO ₄ ·12H ₂ O	88	91	97
	1M NaOH	72	96	73
Rolled	Unexposed	100	100	100
	1M NH ₄ OH	68	76	83
	1M Na ₂ CO ₃	67	100	100
	0.5M Na ₃ PO ₄ ·12H ₂ O	69	100	87
	1M NaOH	65	100	91
Twisted	Unexposed	100	91	100
	1M NH ₄ OH	91	93	92
	1M Na ₂ CO ₃	94	93	100
	0.5M Na ₃ PO ₄ ·12H ₂ O	97	100	88
	1M NaOH	75	78	96

**Table VII - % Retention of Mechanical Properties of LaRC™-TPI After
Exposure to High pH Solutions**

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal	1M NH ₄ OH	80	84	100
	1M Na ₂ CO ₃	97	90	100
	0.5M Na ₃ PO ₄ ·12H ₂ O	78	82	100
	1M NaOH	100	85	100
Rolled	Unexposed	93	94	100
	1M NH ₄ OH	84	95	80
	1M Na ₂ CO ₃	89	95	87
	0.5M Na ₃ PO ₄ ·12H ₂ O	96	99	89
	1M NaOH	82	92	100
Twisted	Unexposed	100	100	100
	1M NH ₄ OH	89	84	62
	1M Na ₂ CO ₃	100	97	80
	0.5M Na ₃ PO ₄ ·12H ₂ O	100	99	82
	1M NaOH	81	75	66

Table VIII - % Retention of Mechanical Properties of LaRC™-CPI After Exposure to High pH Solutions

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal	1M NH ₄ OH	91	94	100
	1M Na ₂ CO ₃	100	100	100
	0.5M Na ₃ PO ₄ ·12H ₂ O	95	88	100
	1M NaOH	100	100	100
Rolled	Unexposed	100	100	100
	1M NH ₄ OH	100	97	83
	1M Na ₂ CO ₃	100	92	97
	0.5M Na ₃ PO ₄ ·12H ₂ O	99	86	97
	1M NaOH	97	86	93
Twisted	Unexposed	95	86	100
	1M NH ₄ OH	100	100	100
	1M Na ₂ CO ₃	100	100	100
	0.5M Na ₃ PO ₄ ·12H ₂ O	100	100	91
	1M NaOH	100	100	96

**Table IX - % Retention of Mechanical Properties of LaRC™-ITPI After
Exposure to High pH Solutions**

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal*	1M NH ₄ OH	80	77	88
	1M Na ₂ CO ₃	100	92	100
	0.5M Na ₃ PO ₄ ·12H ₂ O	93	88	100
	1M NaOH	89	90	100
Rolled**	Unexposed	**		
	1M NH ₄ OH	87	91	82
	1M Na ₂ CO ₃	100	100	92
	0.5M Na ₃ PO ₄ ·12H ₂ O	97	98	94
Twisted**	1M NaOH	83	85	89
	Unexposed	**		
	1M NH ₄ OH	83	84	88
	1M Na ₂ CO ₃	74	75	95
	0.5M Na ₃ PO ₄ ·12H ₂ O	87	84	100
	1M NaOH	90	84	90

* Dianhydride purity 97%.

** Dianhydride purity 98.3%.

Table X - % Retention of Mechanical Properties of HQDEA/4-BDAF After Exposure to High pH Solutions

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal	1M NH ₄ OH	80	87	91
	1M Na ₂ CO ₃	87	93	91
	0.5M Na ₃ PO ₄ •12H ₂ O	70	77	64
	1M NaOH	66	74	87
Rolled	Unexposed	91	91	96
	1M NH ₄ OH	91	86	127*
	1M Na ₂ CO ₃	100	90	137*
	0.5M Na ₃ PO ₄ •12H ₂ O	87	86	104
	1M NaOH	93	92	96
Twisted	Unexposed	100	86	150*
	1M NH ₄ OH	91	89	110
	1M Na ₂ CO ₃	100	100	108
	0.5M Na ₃ PO ₄ •12H ₂ O	100	100	88
	1M NaOH	100	95	127*

* Significant increase in elongation

**Table XI - % Retention of Mechanical Properties of BPDA/3,5-DABTF
After Exposure to High pH Solutions**

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal*	1M NH ₄ OH	99	100	64
	1M Na ₂ CO ₃	100	100	85
	0.5M Na ₃ PO ₄ ·12H ₂ O	93	100	100
	1M NaOH	94	100	79
Rolled**	Unexposed	**	100	35
	1M NH ₄ OH	92	90	100
	1M Na ₂ CO ₃	100	95	100
	0.5M Na ₃ PO ₄ ·12H ₂ O 1M NaOH	96 64	82	37
Twisted**	Unexposed	**	100	27
	1M NH ₄ OH	84	100	100
	1M Na ₂ CO ₃	100	91	61
	0.5M Na ₃ PO ₄ ·12H ₂ O 1M NaOH	80 ***	***	***

* 3,5-DABTF synthesized in house. ** 3,5-DABTF obtained from OXYCHEM (99.9%).

*** Specimens deformed from twisting during exposure.

Table XII - % Retention of Mechanical Properties of 6F/3,5-DABTF After Exposure to High pH Solutions

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal*	1M NH ₄ OH	82	100	72
	1M Na ₂ CO ₃	100	100	100
	0.5M Na ₃ PO ₄ ·12H ₂ O	80	98	71
	1M NaOH	86	98	85
Rolled**	Unexposed	81	90	82
	1M NH ₄ OH	94	89	100
	1M Na ₂ CO ₃	98	93	100
	0.5M Na ₃ PO ₄ ·12H ₂ O 1M NaOH	76	88	75
Twisted**	Unexposed	Broke	during	exposure
	1M NH ₄ OH 1M Na ₂ CO ₃ 0.5M Na ₃ PO ₄ ·12H ₂ O 1M NaOH	100 Broke Specimens	100 during deformed	97 exposure

* 3,5-DABTF synthesized in house.

** 3,5-DABTF obtained from OXYCHEM (99.9%).

Table XIII - % Retention of Mechanical Properties of ODPA/p-PDA After Exposure to High pH Solutions

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal	1M NH_4OH	70	74	74
	1M Na_2CO_3	80	81	81
	0.5M $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	69	73	66
	1M NaOH	74	75	100
Rolled	Unexposed	82	84	62
	1M NH_4OH	89	89	100
	1M Na_2CO_3	94	92	100
	0.5M $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	97	88	100
	1M NaOH	75	94	77
Twisted	Unexposed	Broke	while	attempting
	1M NH_4OH 1M Na_2CO_3 0.5M $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ 1M NaOH	to secure exposure	in clamps	prior to

Table XIV - % Retention of Mechanical Properties of ODPA/3,4-ODA After Exposure to High pH Solutions

Configuration	Solution	Tensile Strength	Tensile Modulus	Elongation
Normal	1M NH ₄ OH	100	98	100
	1M Na ₂ CO ₃	92	94	53
	0.5M Na ₃ PO ₄ ·12H ₂ O	95	94	95
	1M NaOH	95	97	93
Rolled	Unexposed	100	100	26
	1M NH ₄ OH	91	89	100
	1M Na ₂ CO ₃	92	90	100
	0.5M Na ₃ PO ₄ ·12H ₂ O	94	93	98
	1M NaOH	92	90	100
Twisted	Unexposed	100	100	44
	1M NH ₄ OH	90	88	100
	1M Na ₂ CO ₃	100	97	100
	0.5M Na ₃ PO ₄ ·12H ₂ O	87	88	60
	1M NaOH	83	85	92

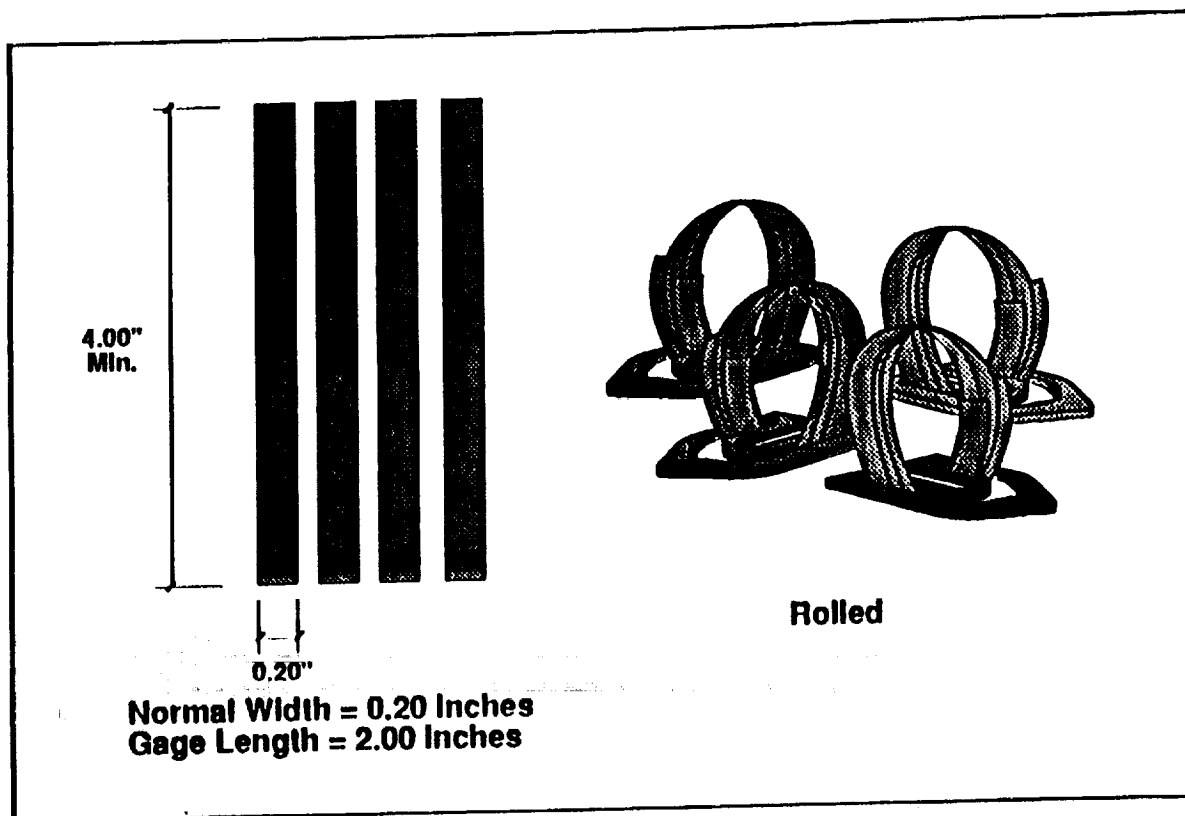


Figure 1- Configurations for chemical exposure

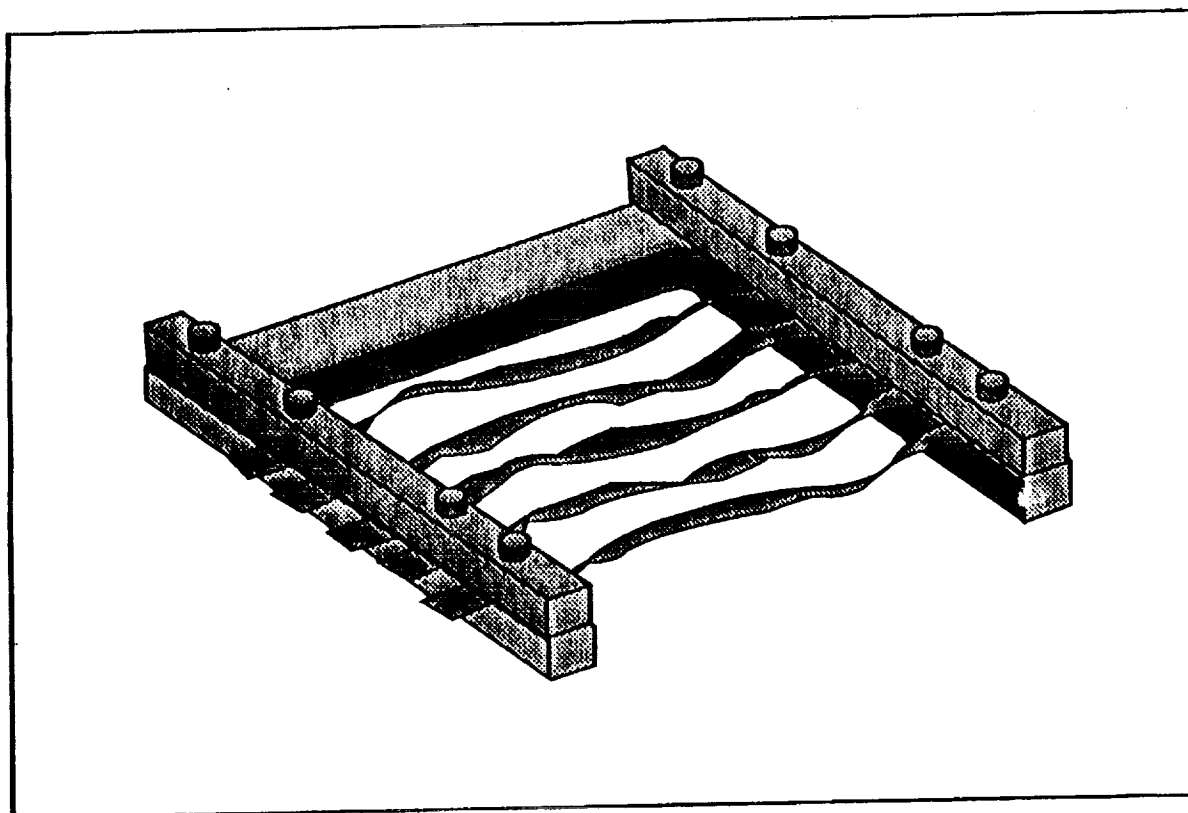


Figure 2- Configuration for chemical exposure

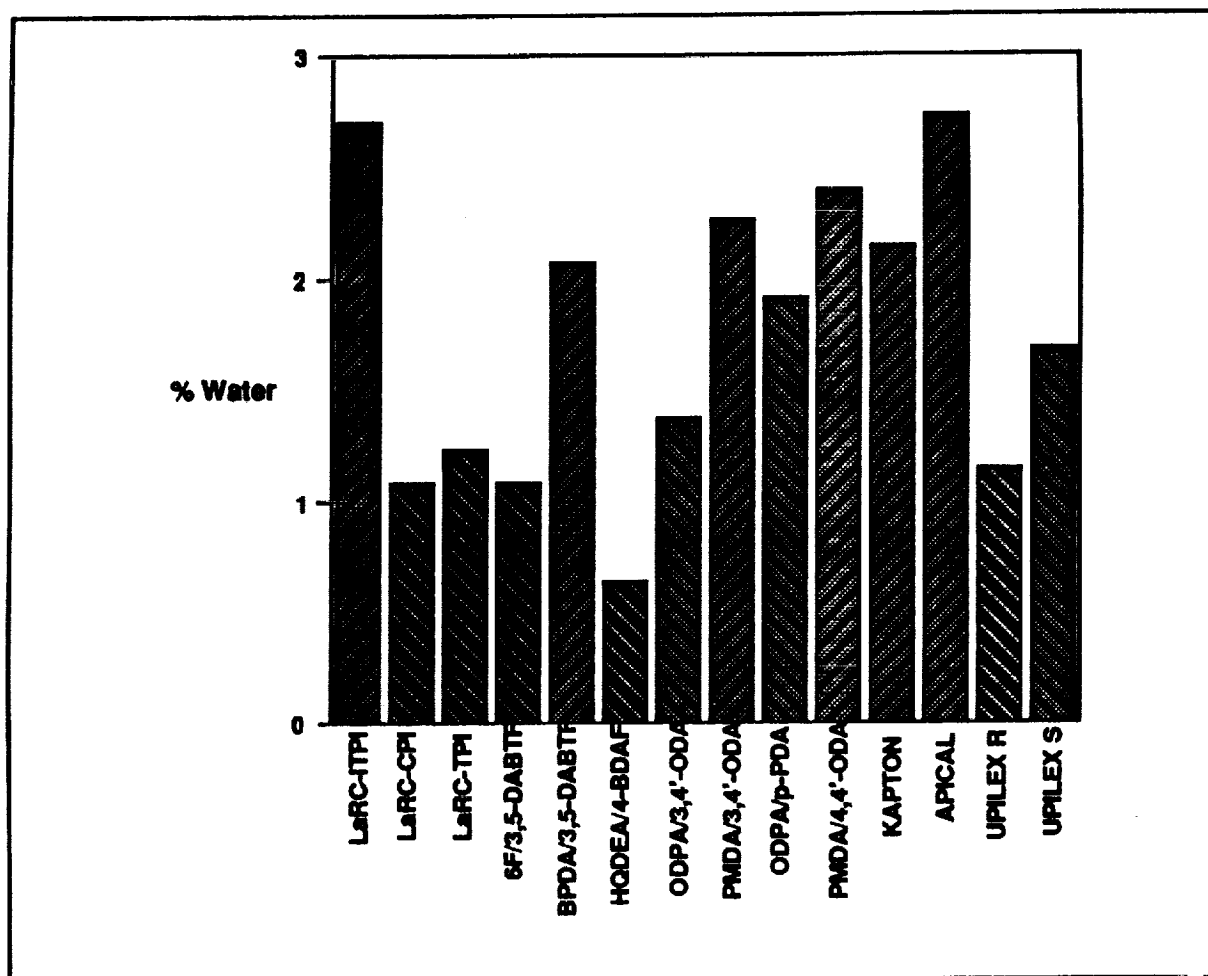


Figure 3 - Moisture Absorption of Polyimides

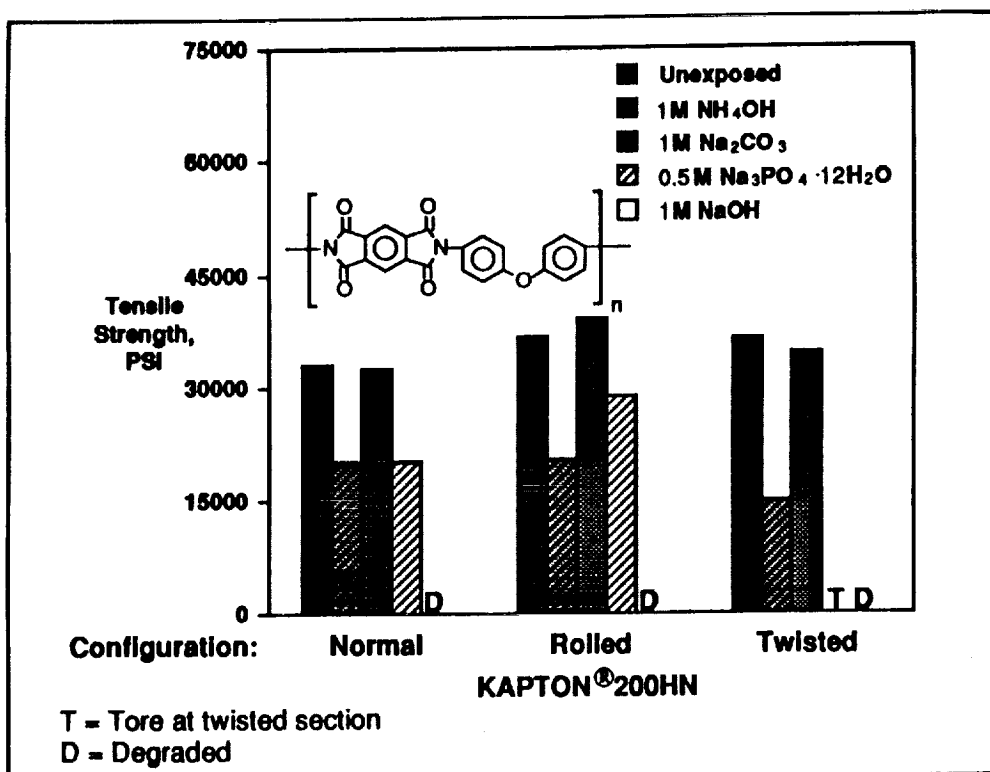


Figure 4 - Tensile Strengths of KAPTON®200HN

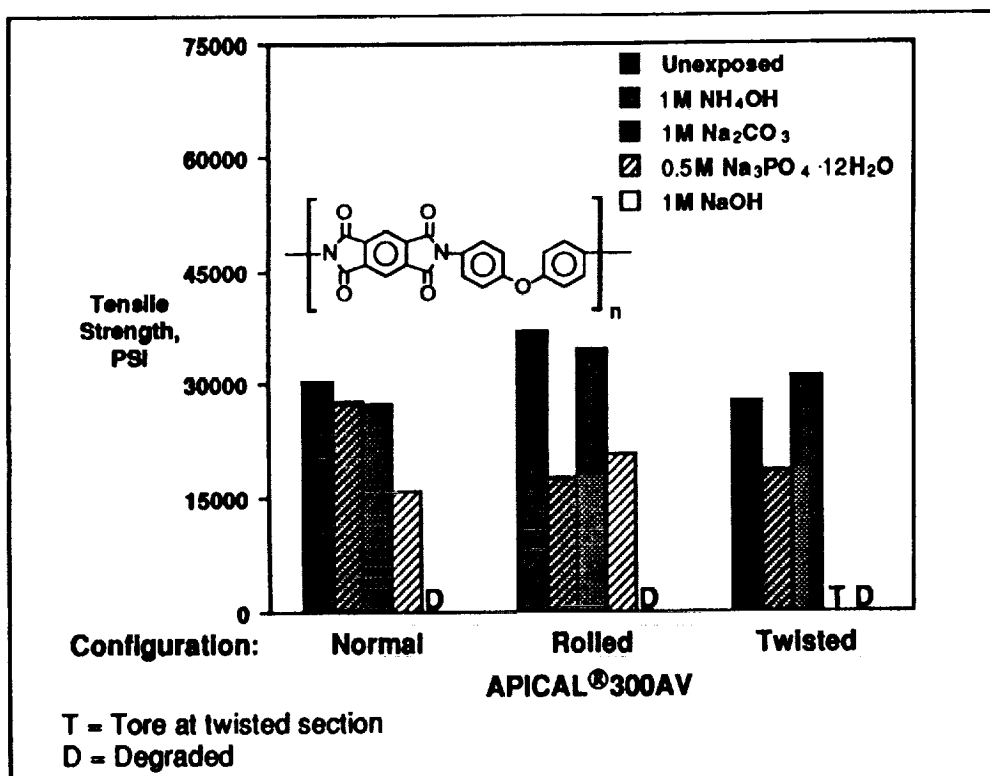


Figure 5 - Tensile Strengths of APICAL®300AV

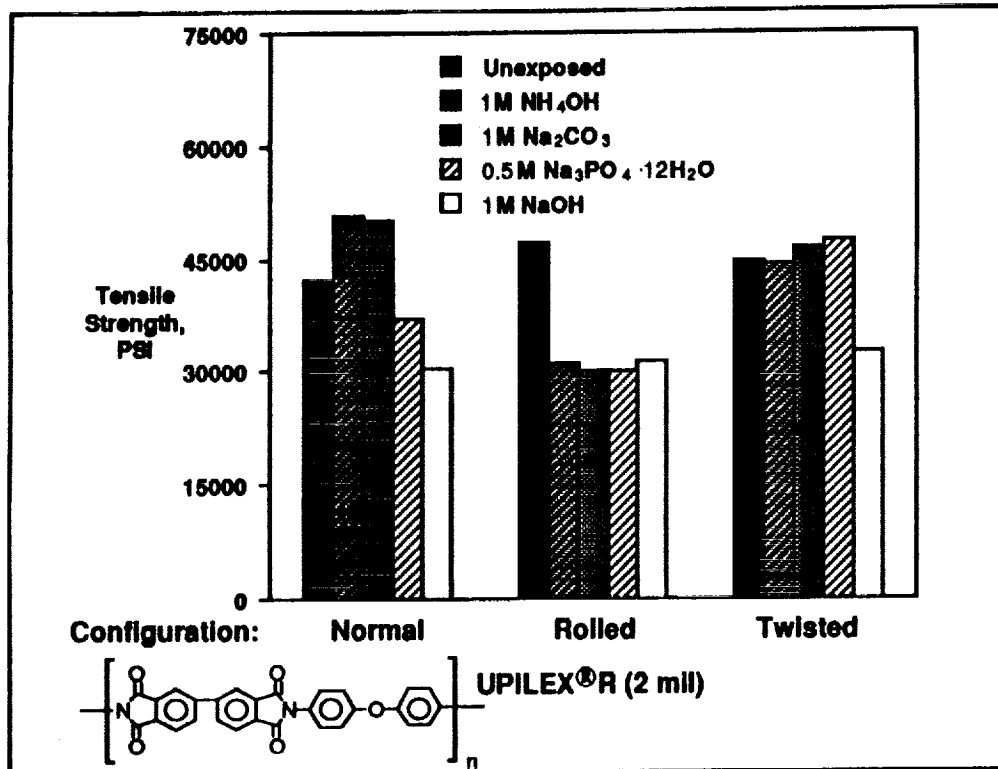


Figure 6 - Tensile Strengths of UPILEX®R

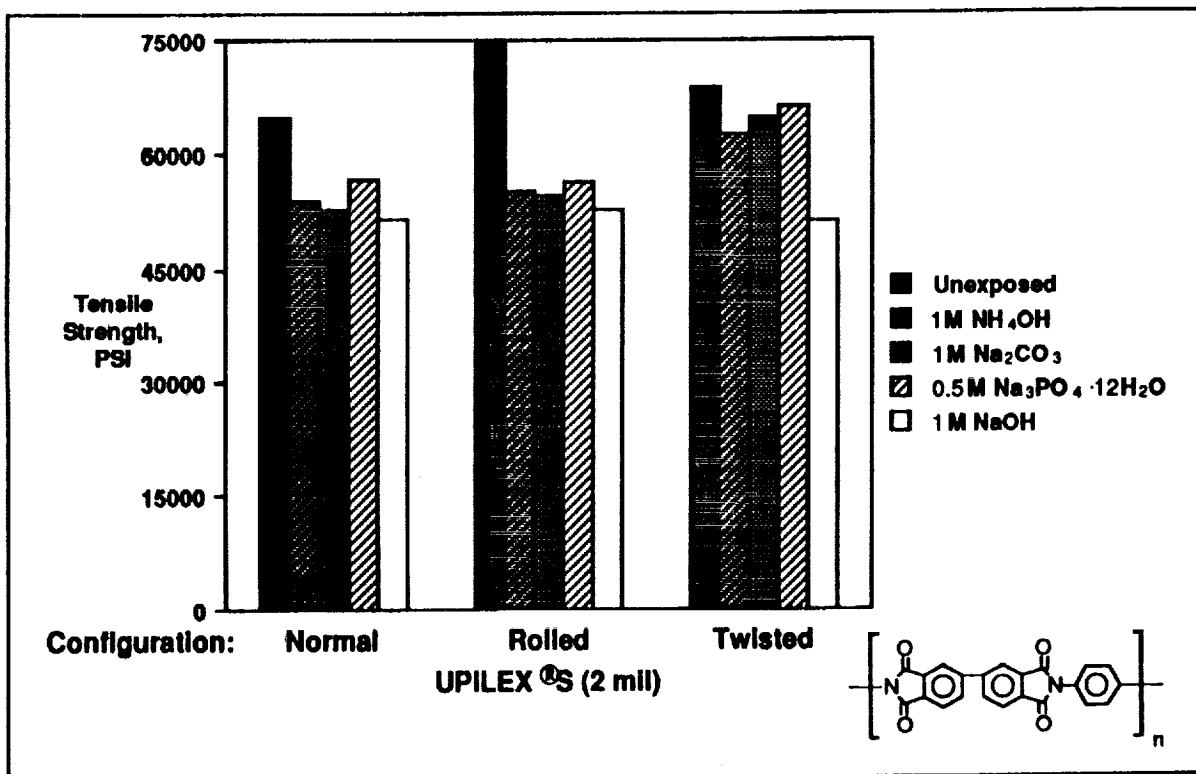


Figure 7 - Tensile Strengths of UPILEX®S

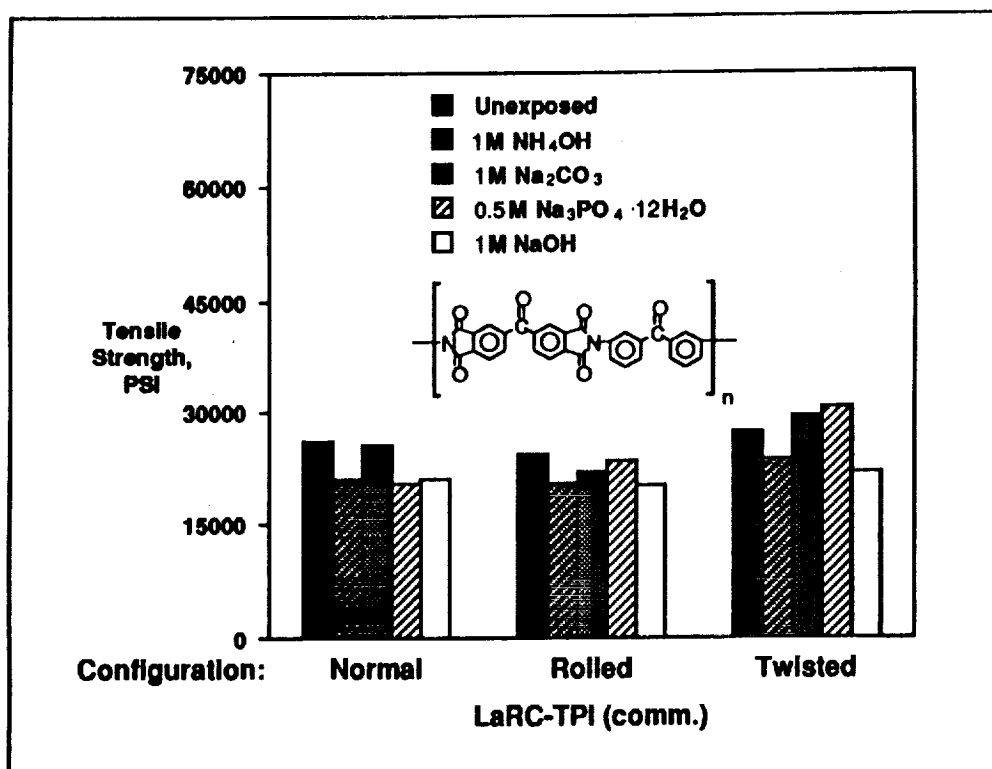


Figure 8 - Tensile Strengths LaRC-TPI

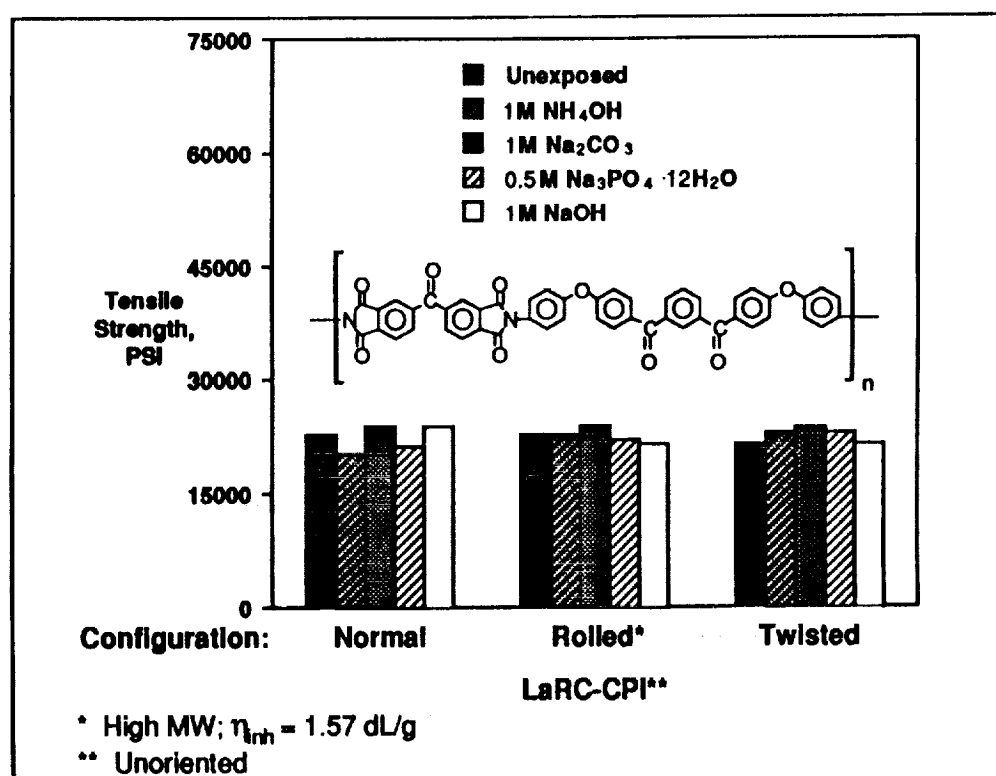


Figure 9 - Tensile Strengths of LaRC-CPI

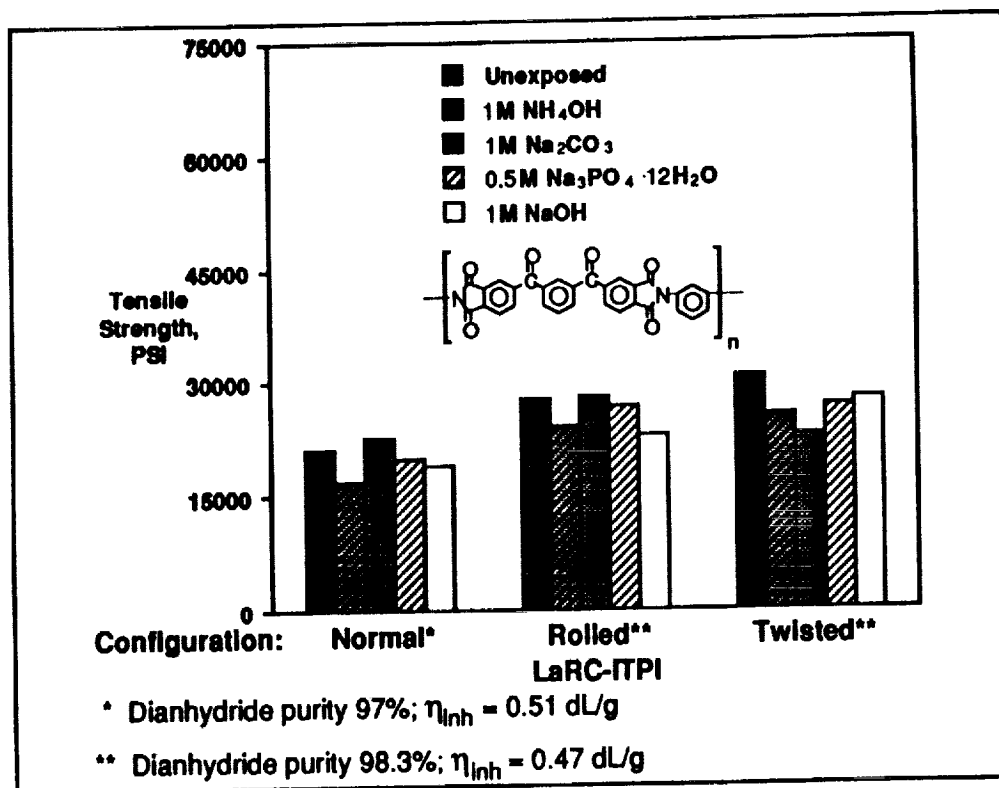


Figure 10 - Tensile Strengths of LaRC-ITPI

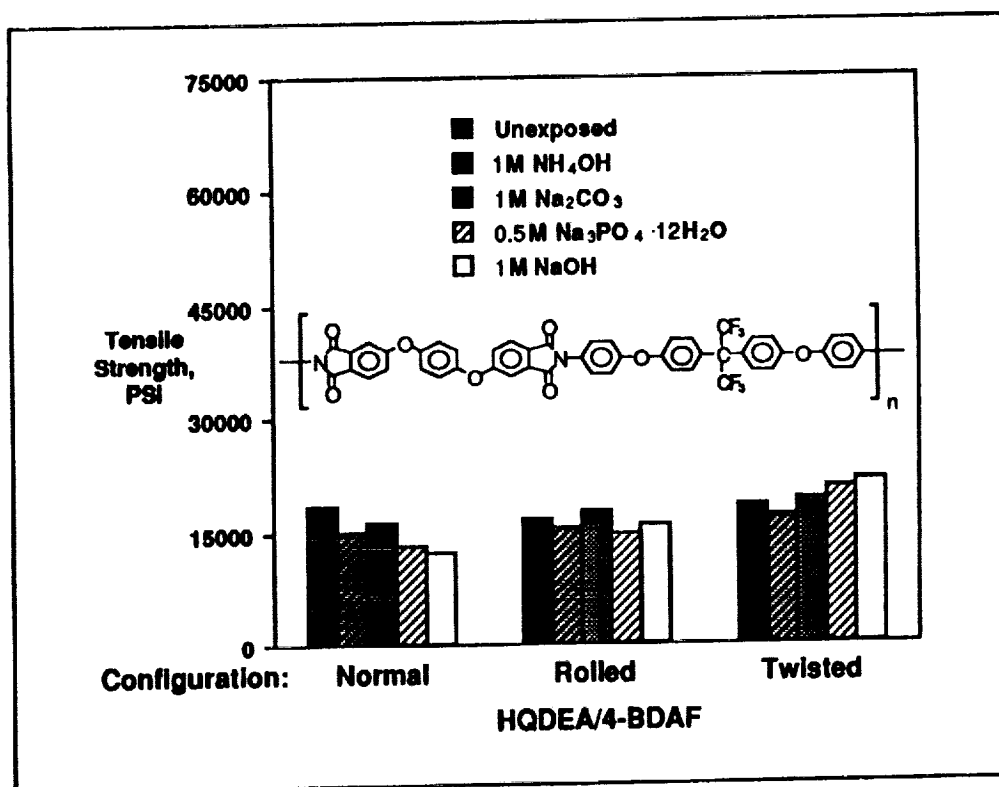


Figure 11 - Tensile Strengths of HQDEA/4-BDAF

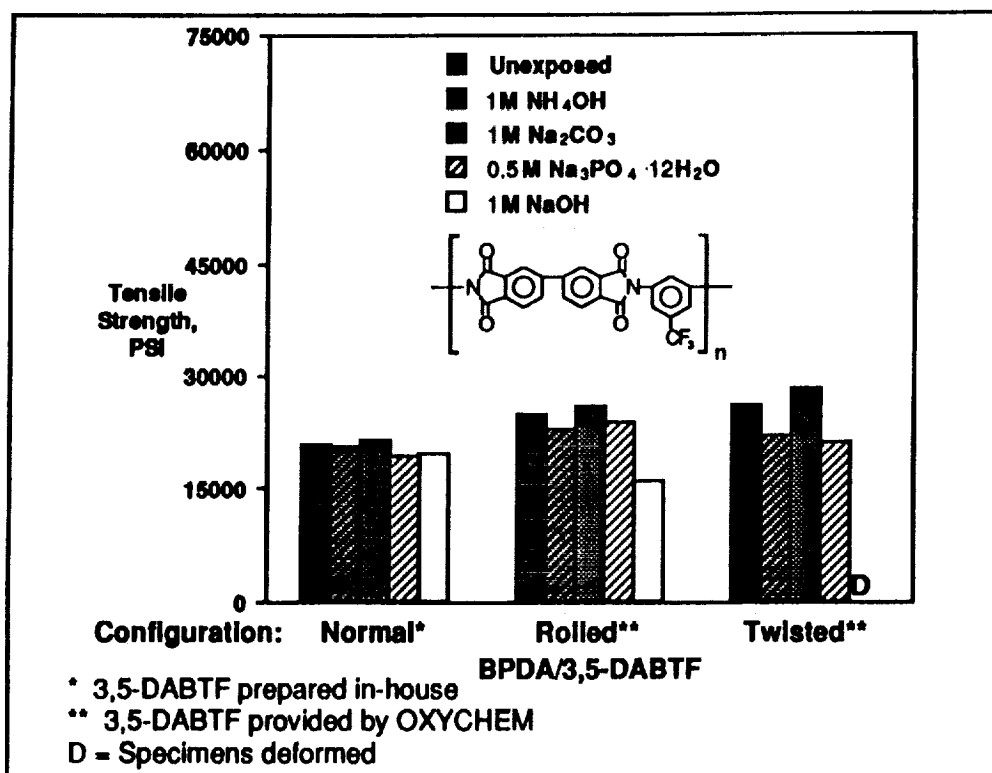


Figure 12-Tensile strengths of BPDA/3,5-DABTF

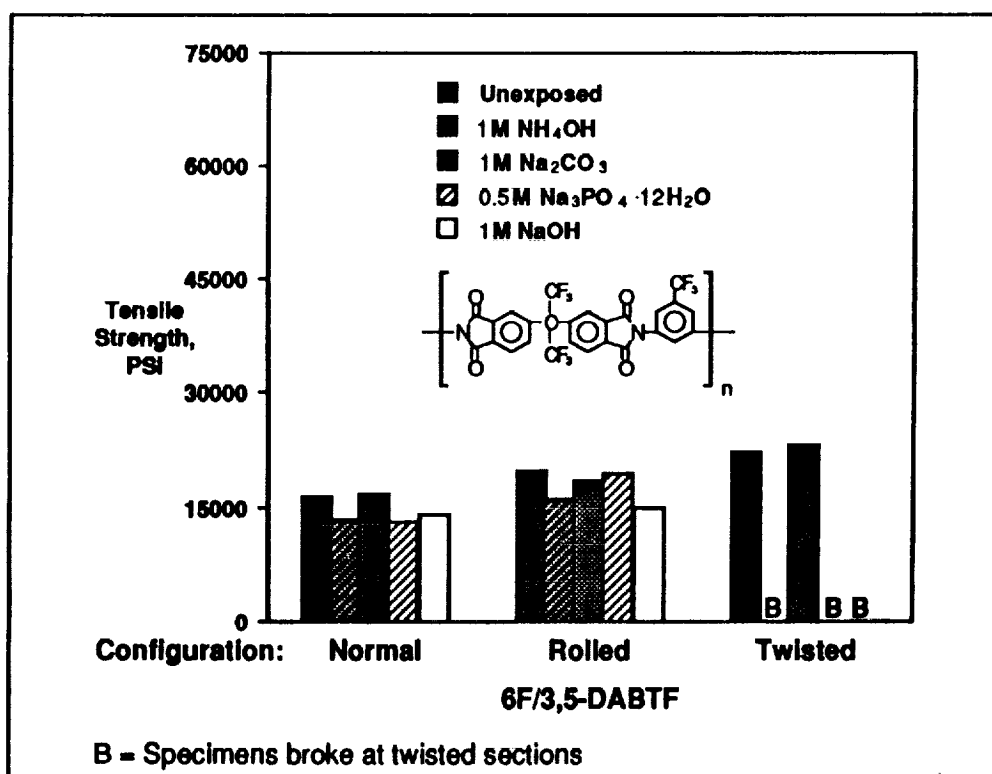


Figure 13 - Tensile Strengths of 6F/3,5-DABTF

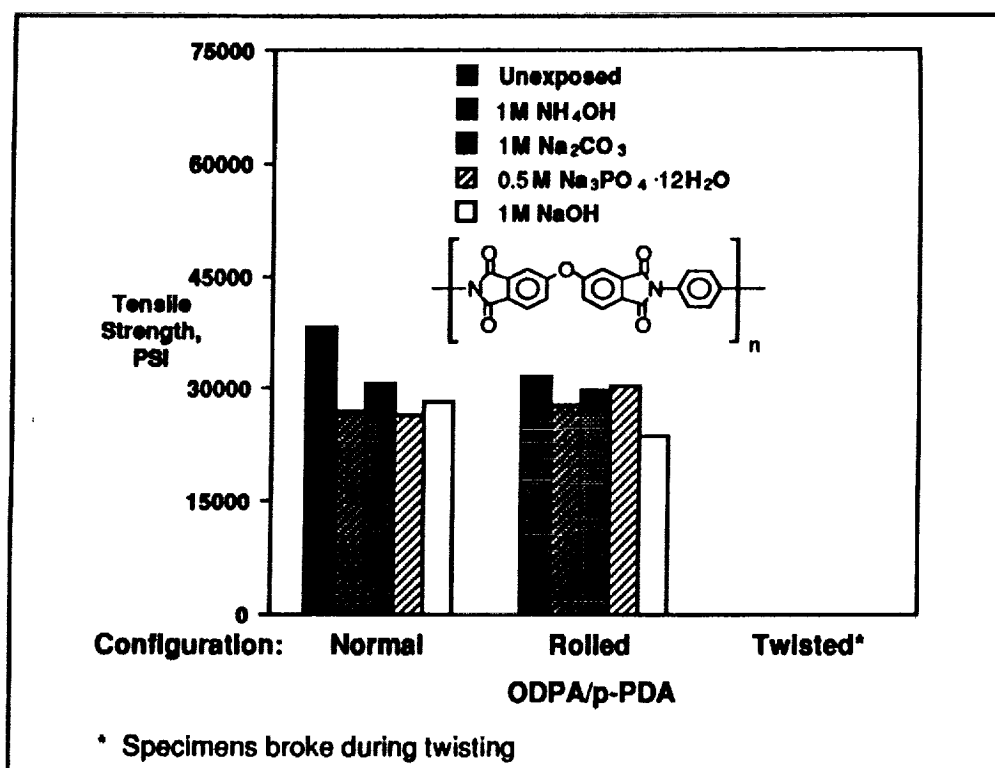


Figure 14 - Tensile Strengths of ODPA/p-PDA

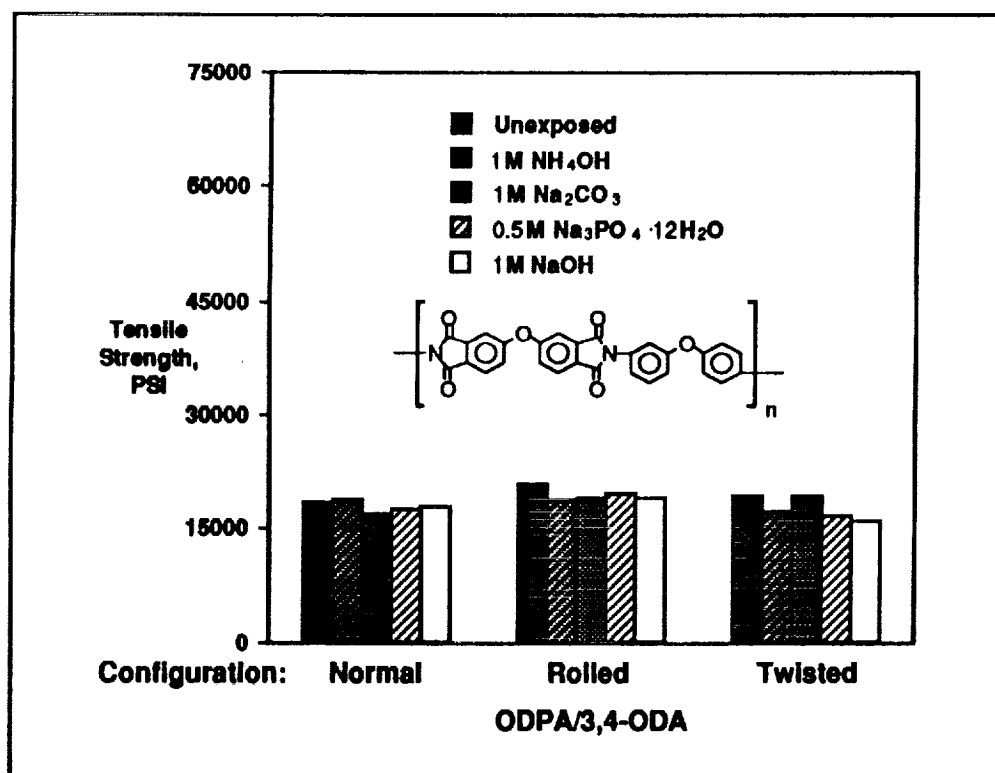
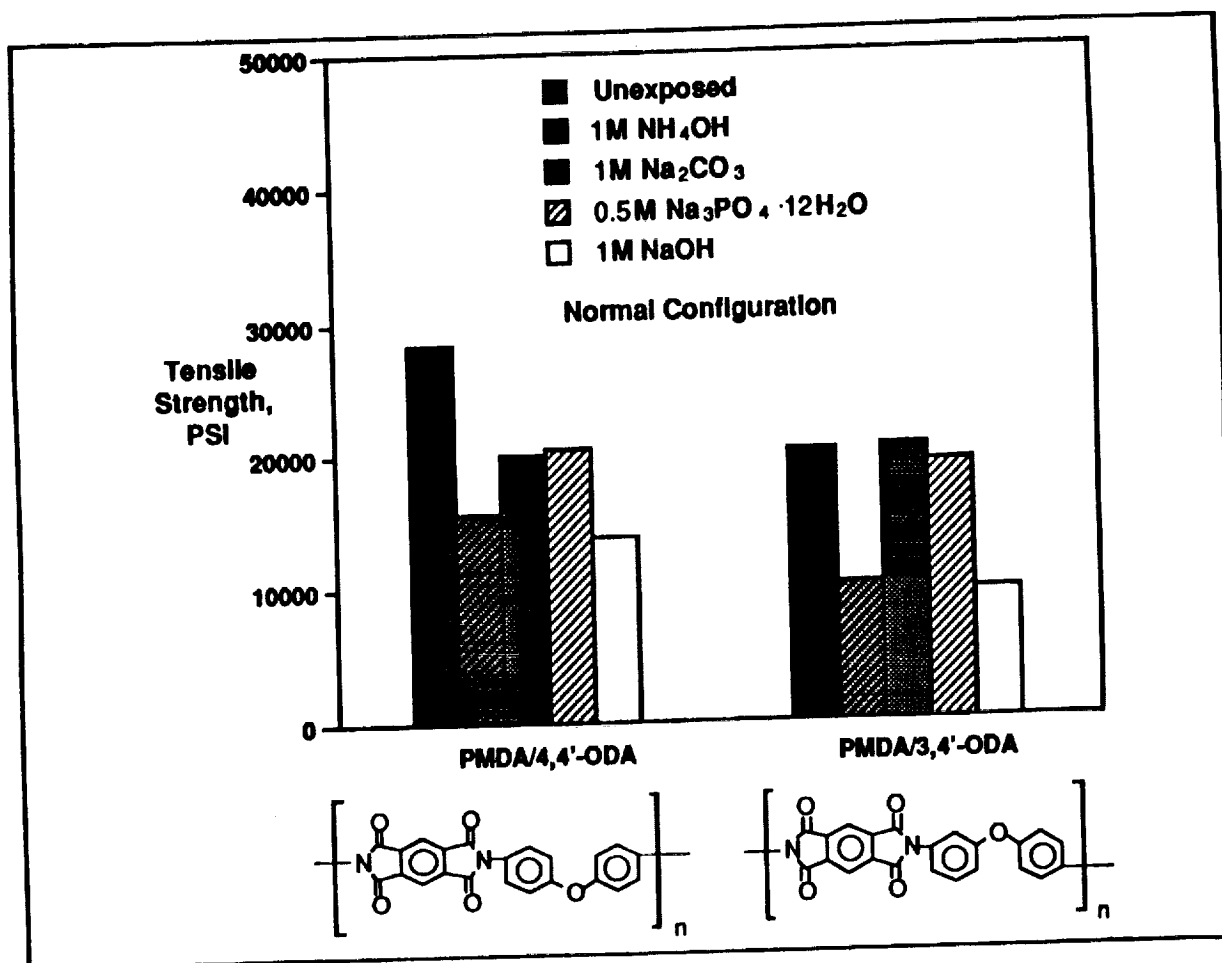


Figure 15 - Tensile Strengths of ODPA/3,4-ODA



REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE January 1992		3. REPORT TYPE AND DATES COVERED Technical Memorandum
4. TITLE AND SUBTITLE The Mechanical Properties of Polyimide Films After Exposure to High pH			5. FUNDING NUMBERS WU 506-43-11	
6. AUTHOR(S) Catharine I. Croall and Terry L. St. Clair				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) NASA Langley Research Center Hampton, VA 23665-5225			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-104202	
11. SUPPLEMENTARY NOTES Use of trade names or manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Unclassified-Unlimited Subject Category - 27			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Wiring failures linked to insulation damage have drawn much attention in the aerospace industry and concerns have developed regarding the stability and safety of polyimide insulated electrical wire. Several polyimides were selected for evaluation for resistance to degradation by various aqueous alkaline solutions. The polyimides under evaluation include commercially available films such KAPTON®, APICAL®, LaRC™-TPI and UPILEX®R and S, as well as a number of experimental films prepared at NASA Langley Research Center. Thermally imidized films were studied for their retention of mechanical properties after exposure to high pH solutions under stressed conditions.				
14. SUBJECT TERMS Polyimide Film properties, Polyimide, Hydrolysis, and Aircraft Wire Insulation			15. NUMBER OF PAGES 32	
			16. PRICE A05	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	