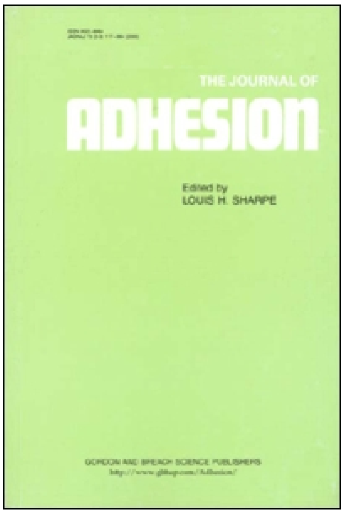

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Improving Bonding to Piezoelectric Poly(vinylidene fluoride) for Sensor Applications*

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Argon, oxygen, nitrogen and ammonia plasmas and an acid etch pretreatment were performed on uniaxially stretched piezoelectric poly(vinylidene fluoride) film in order to improve wettability and bonding. Oxygen plasma was found to be too harsh, but nitrogen and argon plasmas improved wettability and resulted in a seven-fold increase in 180° peel strengths. However, this improvement in peel strength was accompanied by a 90% decrease in the piezoelectric properties of the polymer. The acid etch yielded contact angles similar to those of the plasma treated material, and improved peel strengths some twelve times over that of the untreated film. Significantly, no piezoelectric loss resulted from the acid etch.

KEY WORDS poly(vinylidene fluoride); wettability; plasma pretreatment; failure loci; polymer acid etch; piezoelectric polymers; peel strength; XPS analysis; contact angle; strain energy release rates.

INTRODUCTION

Piezoelectric poly(vinylidene fluoride) (PVF_2) film has been successfully employed in adhesive joints to measure peel stresses within the bondlines of laboratory specimens.[1,2] Multi-point sensors are created and bonded into adhesive joints in order to measure the peel stress gradients. Because these sensors are *in situ*, within the bondline, it is important to obtain good bonding to the PVF_2 surface in order to maintain the bond strength. Because PVF_2 has a low surface energy, chemical modification of the surface should improve the wettability of the film and, thus, bonding to the film. Physically abrasive techniques are unattractive, as such methods would destroy the sensors.

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An important chemical surface modification technique is plasma treatment. Plasma is spatially neutral ionized gas. A plasma pretreatment can alter solid material surfaces in five ways: 1) surface cleaning, 2) ablation, 3) crosslinking, 4) surface activation and 5) incorporation of plasma constituents. While solvent cleaning methods tend to leave an organic contaminant that may interfere with adhesion, the free radical chemistry involved in plasma pretreatments cleans surfaces very well. When pretreating polymers, plasmas are capable of not only cleaning the surface but ablating, or microetching, the surface by breaking organic bonds. In fact, inert gas plasmas have sufficient energy to break the strongest organic bond, thus allowing the processes of ablation, crosslinking and surface activation to occur.[3] After plasma pretreatments polymeric surfaces remain activated and can react with air upon exposure, incorporating oxygen into the surface.[4,5] The incorporation of plasma constituents has been shown by Hollahan, Stafford, Falls and Payne,[6] who observed that amine groups were incorporated into several polymer surfaces upon exposure to ammonia and nitrogen/hydrogen plasmas.

Momose, Noguchi and Okazaki used plasma pretreatments of argon and oxygen to increase the surface energy of unstretched PVF_2.[7] After treatment times of 60 seconds, contact angles between 26° and 30° were obtained. The measured contact angles after pretreatment represent a 60% reduction from the 88° angle of the untreated PVF_2. Tetrafluoromethane and tetrafluoromethane/oxygen plasmas were used to lower the surface energy, resulting in contact angles between 93 and 126°. In their study, no adhesion tests were performed on the treated PVF_2 in order to correlate increased wettability to improved bonding.

Much more work has been done in the area of bonding to poly(tetrafluoroethylene) (PTFE) than in bonding to PVF_2.[8] Two chemical modification methods, plasma pretreatment and acid etching, have been investigated to improve bonding. Experiments with ammonia plasma have shown that T-peel strengths of PTFE bonded to nitrile rubber improved by only a small percentage when pretreated.[9] Inagaki, Tasaka and Kawai found that the adhesive side of the failure surface was contaminated with a waxy substance. They postulated that low molecular weight oligomers were formed on the PTFE surface during the plasma pretreatment which were weakly attached to the bulk. Thus, the fairly low failure strength was reportedly due to a weak low-molecular-weight PTFE/bulk PTFE interphase. It is interesting to note that the ammonia plasma treatment reduced the advancing contact angle of water on the PTFE from 118 to 16°. This is a good example of the axiom that wettability is a necessary but insufficient condition for achieving good bond strengths. Thus, eliminating the formation of low molecular weight surface species, or increasing the cohesive strength of the fluorocarbon surface, is needed in addition to surface cleaning and increasing the surface energetics of PTFE films.

Another class of surface chemical-modification technique that has been shown to improve bonding to PTFE surfaces is etching techniques. The best example is the use of metallic sodium in the etching of PTFE surfaces.[10] Metallic sodium in a tetrahydrofuran solution has been used to etch PTFE surfaces leaving a higher energy surface with no weakened surface layer.

The present work is a study of the use of plasma treatment and acid etching to improve adhesive bonding to PVF_2 surfaces. Both wetting and bonding were measured in order to investigate both decreases in surface energy of the fim and improved adhesion. The effects of the pretreatments on the piezoelectric properties of the film were also investigated.

EXPERIMENTAL

Surface Pretreatment and Contact Angle Measurements

The PVF_2 film used in this study was KYNAR® piezoelectric film manufactured by Atochem (formerly Pennwalt). The film was 52 μm thick, and a 400–700 Å layer of constantan, a copper-nickel alloy, was sputtered on both PVF_2 surfaces during production in order to aid in the poling of the film. Film poling is a method of electrically aligning the CH_2-CF_2 repeating units to make the film piezoelectric by subjecting the film to a high electrical field at elevated temperatures. Prior to the piezoelectric poling, the film is uniaxially stretched to a draw ratio between 4 and 5. At these high draw ratios, minor variations in the amount of polymer stretching would not be expected to cause significant variations in the degree of polymer crystallinity. Thus, it is expected that surface pretreatments would create reproducible bonding surfaces in the commercial KYNAR® film. The metal was chemically etched from the PVF_2 surface using a dilute ferric chloride circuit board etchant prior to solvent cleaning and plasma pretreatments. In order to insure that no surface modification resulted from the ferric chloride, control samples obtained from Atochem without sputtered metal were also tested. A complete summary of pretreatments and surface preparations employed in this study is listed in Table I.

Acetone, water, methanol and a 50% methanol–50% water mixture were investigated as surface cleaning methods. Water-drop contact angles were measured on the solvent wiped surfaces to determine wettability. The methanol wipe reduced the contact angle the most, from 78 to 55°. Thus, all film samples were solvent wiped with methanol prior to further pretreatment or bonding, except in the case of the acid etch pretreatment. The contact angles for the film wiped with acetone, water

TABLE I
Summary of pretreatments. Dashes link prior common steps with following groups, e.g. all plasma treated films were previously metallized film, etched with ferric chloride and solvent-wiped with methanol

Metal	Etching Solution	Cleaning Solvent	Plasma Treatment
No			
Yes —	Brite Dip		
	Ferric Chloride —	Water	
		Acetone	
		Methanol/Water	
		Methanol —	Oxygen
			Nitrogen
			Argon
			Ammonia
			N_2/Ammonia
			Ar/Ammonia

and the methanol-water mixture were 65, 72 and 79°, respectively. All immediately advancing contact angles were measured using a Rame-Hart #100-00 115 NRL goniometer telescope.

Following the metal removal by ferric chloride etching and surface cleaning by a methanol wipe, the PVF_2 film was subjected to oxygen, argon, nitrogen and ammonia plasmas in a Plasmod (manufactured by Tegal Corporation) which generates a radio-frequency (13.56 MHz) 50 watt plasma at 1.2 torr. A simple schematic diagram of the plasma reactor system is shown in Figure 1. Gas flow rates were in excess of 5000 ml/min. The PVF_2 films were placed for treatment in the end of the chamber nearest the vacuum outlet. Previous studies showed that the plasma reactivity is highest in this region of the chamber.

Contact angle specimens were one inch by two inches (25.4 × 50.8 mm) from which all of the metallized layer was removed from only half of the specimen. This was done to insure applicability of the pretreatment to piezoelectric stress sensors which contain small regions of metallization. The specimens were pretreated for various time periods, and the contact angles were measured within three minutes of removal from the plasma. Pretreatment exposure times were between 10 and 300 seconds.

An acid etch, using Brite Dip, was also investigated as a surface chemical modification technique to increase the surface energy of the PVF_2 and improve bonding to the film surface. Brite Dip is a solution consisting of 70% acetic acid, 26% phosphoric acid and 4% nitric acid, all of which are in concentrated form (98% or greater). The metallized film was dipped into an 80% aqueous solution of the Brite Dip since it was found that the undiluted solution removed the metal within seconds, and a more controlled metal removal was desired. At the other extreme, a 60% solution did not remove the metal after a five-minute exposure. The 80% Brite Dip solution removed the metal in 45 seconds, and the film was treated for one minute.

XPS Studies

Elemental concentrations on the surfaces of the untreated and pretreated films were determined using a Perkin-Elmer PHI 5300 spectrometer which employs a MgK_α (1253.6 eV) achromatic X-ray source. The source operated at 14 keV with an emission current of 20 mA. Pressure less than 2×10^{-7} torr was maintained throughout the analysis. Measurements were made at a 45° incident angle.

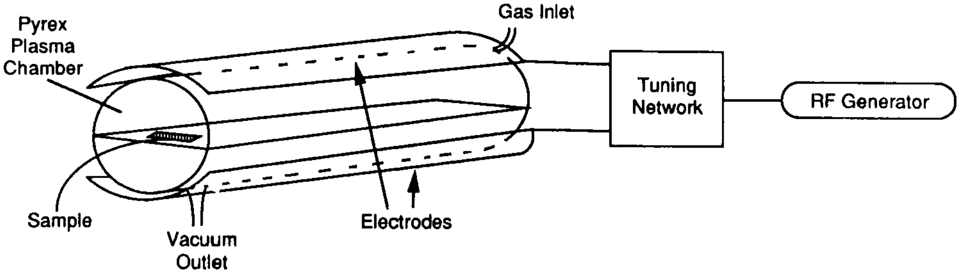

FIGURE 1 Schematic of Plasmod reactor system.

Peel Tests

In order to assess the improvement in bonding to the PVF_2 surfaces, 180° peel specimens were made using film that had been pretreated with various plasmas (following ferric chloride metal etch and methanol washing) and the acid etch. All bonding to the pretreated surfaces was performed within three minutes of the final pretreatment in order to obtain the maximum benefit from the pretreatment. The films were bonded to grit-blasted 6061–T6 aluminum substrates with a commercial two-part amine-cured epoxy. The adhesive thickness was about 0.15 mm (minimum bond thickness controlled by a clamping pressure of about 75 kPa), and testing was performed at ambient conditions (20°C and 40% relative humidity). Measurements were made using a 3M90 peel/friction testing device from Instrumentors, Inc. All peel tests were made at 0.3 in/min and averaged over 10 seconds. There was very little variation in peel strength from the average over the testing time due to the elastic nature of the PVF_2 film.

Failure Loci

In order to determine the average failure plane in the peel specimens, the elemental concentrations of the two failure surfaces were determined using XPS. The equipment and procedure for the failure loci study were the same as used in the initial XPS study.

Tapered Double Cantilever Beam Tests

In order to assess any bond weakening due to imbedded piezoelectric sensors, pretreated film was also bonded into the bondline of 12.7 mm wide tapered double cantilever beam (TDCB) specimens. The TDCB specimen is suggested in the literature by Mostovoy and Ripling as a fracture mechanics specimen whose strain energy release rate is independent of crack length.[11,12] Thus, strain energy release rate is directly proportional to the square of the critical force necessary to propagate the crack. Care was taken to initiate a sharp crack into the bondline prior to testing the specimen. This was accomplished by clamping the specimen just beyond the beginning of the taper and driving a wedge into the loading end of the specimen. In this way a crack was initiated which propagated to the region of the clamp. The clamp was then removed prior to testing the TDCB. A schematic drawing of the TDCB specimen employed in the study is shown in Figure 2.

The imbedded pretreated film extended from the beginning of the taper to the center of the taper across the specimen width. Initial cracks were always propagated past the start of the imbedded film by placing the clamp just past the initial taper section. By imbedding the film in only the first half of the joint length and testing the entire joint length, the fracture energy with and without the imbedded film was determined for each specimen.

A two-part amine-cured epoxy adhesive was employed in the specimens. The adhesive thickness was held constant for all specimens at 0.4 mm (0.015 in) using spacers in both ends of the specimen. The loading rate was also held constant at 0.125 mm/min (0.005 in/min). Both 45-second argon plasma treated films, the

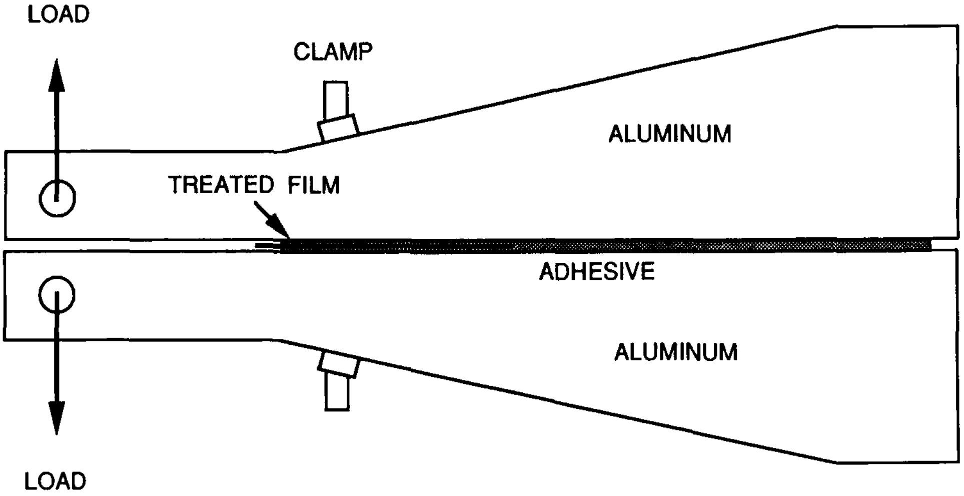

FIGURE 2 Schematic of clamped tapered doubled cantilever beam specimen employed in bonding studies.

plasma treatment resulting in the highest peel strength, and the 80% Brite Dip etched films were studied. As a control, untreated films were also imbedded into a TDCB bondline.

Measurements of Piezoelectric Properties after Pretreatment

In order to determine the effect of the pretreatments on the piezoelectric properties of the film, pretreated PVF_2 films containing one stress sensor were bonded into epoxy butt joints. The joints were then cyclically loaded, and the produced voltages from the stress sensor were measured. Three specimens were employed. They included: a non-pretreated control specimen, a specimen treated with argon plasma for 45 seconds, and a specimen etched in the 80% Brite Dip solution for one minute.

RESULTS AND DISCUSSION

Results from the contact angle measurements are shown in Figure 3. It was found that the oxygen plasma was far too aggressive, especially for the metallized surfaces. With treatment times of only 15 seconds, the PVF_2 between the metal surfaces relaxed from the stretch it received prior to poling. The polymer relaxation caused ridges in the metallized layer where the metal delaminated from the PVF_2. The authors attribute the relaxation to heat produced as the oxygen plasma oxidized the sputtered metal. The oxidation was evident in discoloration of the metal. The heat produced by the oxidation would be quickly transferred to the PVF_2 film due to the minimal thickness of the metal layer and high thermal conductivity of the metal surface. It should be noted that the PVF_2 without metallization was not visibly affected by the oxygen plasma after plasma treatment times of 60 seconds. The

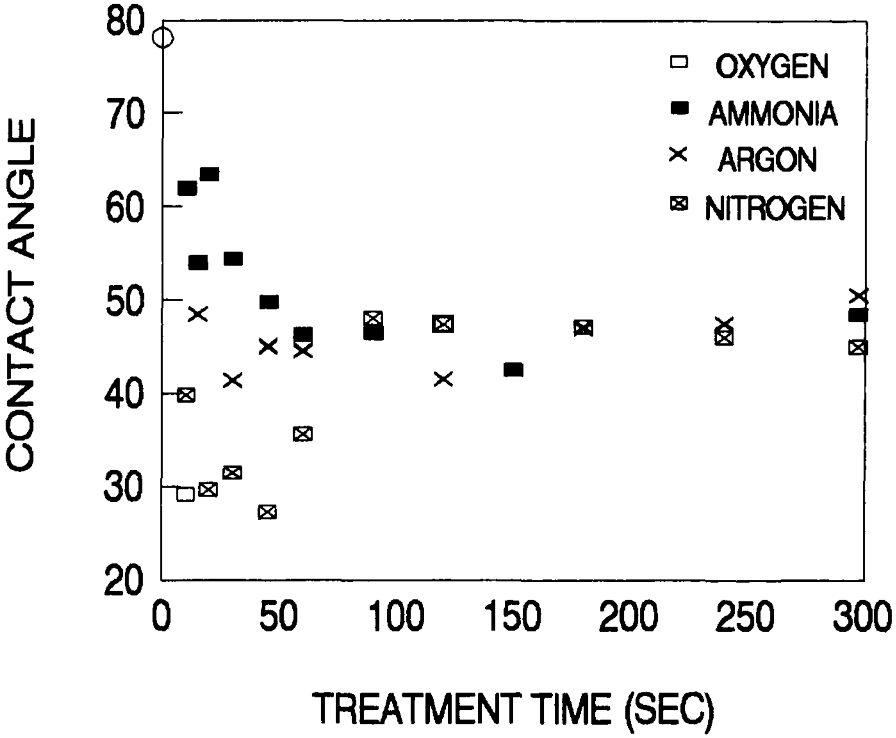

FIGURE 3 Water contact angle measurements as a function of plasma exposure time.

wettability of the PVF_2 surface after only a 10-second exposure was the best of any pretreatment employed. However, since piezoelectric loss will occur at temperatures well below that necessary to cause stretch relaxation, the oxygen plasma was deemed inappropriate for sensor applications. Importantly, there is no evidence to suggest that the treatment could not be used effectively to improve wettability of non-metallized PVF_2.

Ammonia and argon plasma pretreatments of the PVF_2 surface produce contact angles between 45 and 50°. Surprisingly, between 20 and 45 seconds pretreatment time in the nitrogen plasma, the contact angle goes through a minimum at 27°. Thereafter, the contact angle rises to the same level as argon and ammonia pretreatments. This could be attributable to excessive bond breaking on the PVF_2 surface which could create a rough micro-surface, resulting in an increased contact angle. As the PVF_2 surface has a contact angle of 55° after the methanol solvent wipe, all plasma environments employed reduced the contact angle and, thus, improved the wettability of the PVF_2.

Although the film was not visibly damaged in the argon, ammonia or nitrogen plasmas and no visible relaxation was observed at treatment times of up to 300 seconds, the temperature in the specimen containment vessel did increase considerably. This temperature rose to about 120°F (50°C), which is near the point at which time-dependent piezoelectric loss in the PVF_2 begins (60°C). The film could be heating more than that with the reactions that take place on the film surface; therefore, it is conceivable that some piezoelectric loss may occur during lengthy plasma pretreatments. In addition, excessive plasma pretreatment would be expected to create a weakened surface layer of the polymer due to ablation, which has been observed with PTFE.[9] In order to reduce the possibility of piezoelectric loss and to minimize PVF_2 ablation, and noting that no statistically significant changes occur in surface contact angles after two minute pretreatments, pretreatments for the bonding study were held to two minutes or less.

The resulting contact angle for the acid etched surface was 47.5°. This compares well with the plasma treated film, with the exception of the minimum observed with nitrogen plasma, and represents a reduction in comparison with the methanol wipe alone.

A summary of the pretreatment results is shown in Figure 4. All pretreatments reduced the contact angle of water on the PVF_2. The most significant reduction, representing a reduction of two-and-a-half times, was observed on methanol-wiped film treated for 45 seconds in nitrogen plasma. Oxygen plasma also greatly increased

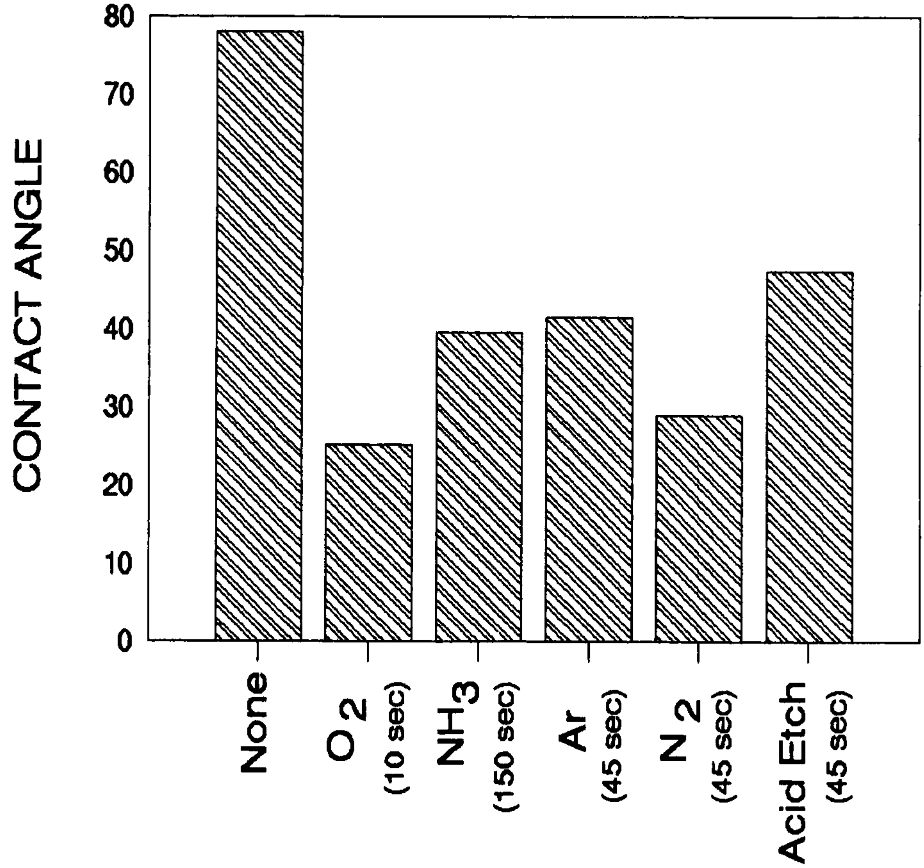

FIGURE 4 Summary of minimum water contact angle measurements for all pretreatments studied. Pretreatment times are shown in parentheses.

TABLE II
Elemental concentrations from XPS analysis of pretreated PVF_2 films

Pretreatment	Atomic Concentration (%)						
	C	O	N	F	Cu	Ni	P
None	62.9	17.0	1.3	13.2	3.3	2.3	nil
Nitrogen Plasma	51.4	13.0	1.4	33.2	0.2	0.8	nil
Argon Plasma	52.5	20.8	1.1	20.9	0.4	4.3	nil
Ammonia Plasma	63.4	9.2	6.8	20.5	0.0	0.1	nil
Acid Etch	58.8	7.3	1.2	32.5	0.1	0.1	0.0

wettability but was found to cause relaxation of the stretched polymer between the metallized layers. Thus, it was determined to be inappropriate for sensor applications.

The XPS results shown in Table II represent treatment times of two minutes following metal removal and methanol cleaning. The presence of minute amounts of copper and nickel on the untreated surface is consistent with the composition of the metallized surface of the KYNAR® film which, apparently, is not completely removed by the dilute ferric chloride solution. The metal content on the surface is reduced following any of the plasma treatments and the acid etch. The oxygen content on the surface of the control samples could be associated, in part, with the surface oxide of the remaining metal alloy. Unfortunately, no XPS was performed on virgin PVF_2 film which had not been metallized. Such analysis may have supported this hypothesis for the presence of the oxygen on the tested samples.

Elemental ratios of carbon-to-fluorine and nitrogen-to-carbon are shown in Table III. Since most surface contaminants are organic species, surface cleaning by the plasma would be expected to reduce the carbon-fluorine ratio toward the value of one which would be expected from a "perfectly clean" PVF_2 surface. This trend is confounded, however, by the fact that plasma treatments are also expected to cause defluorination of the PVF_2[9] which would tend to increase the carbon-to-fluorine ratio. Thus, one would not expect to obtain a ratio of one experimentally, and the ratio would be expected to go through a minimum at the point at which the surface cleaning is maximized and the defluorination is minimized. Theoretically, then, a lower carbon/fluorine ratio would be expected to produce a better bonding surface.

The nitrogen-to-carbon ratio is indicative of the incorporation of nitrogen into the surface, either from the nitrogen in the air reacting with activated species after

TABLE III
Comparison of carbon-fluorine and nitrogen-carbon surface elemental ratios

Pretreatment	$\frac{C\%}{F\%}$	$\frac{N\%}{C\%}$
None	4.8	0.021
Nitrogen Plasma	1.5	0.027
Argon Plasma	2.5	0.021
Ammonia Plasma	3.1	0.107
Acid Etch	1.8	0.020

the pretreatment or from ammonia nitrogen incorporation during pretreatment. Nitrogen incorporation due to post-treatment exposure to air seems unlikely as there appears to be significant incorporation only in ammonia-treated samples. This is also supported by the work of Engelman and Yasuda[13] who observed no nitrogen incorporation in plasma treated polymers due to post-treatment atmospheric exposure. Ammonia nitrogen incorporation could lead to improved bonding as the nitrogen is suspected to be in the form of amine groups which could chemically react with the epoxide rings in the adhesive. This supposition is supported by the work of Hollahan, *et al.*[6] Interestingly, all other pretreatments lead to a decrease in surface nitrogen content.

It is also of interest to note that the acid etched surface contained no phosphorus. This eliminates a possible surface residual from the phosphoric acid in the Brite Dip which was initially considered as a possible cause of the improvement in wetting of, and bonding to, the acid-etched PVF_2.

The results of the peel strength measurements are shown in Figure 5. Samples obtained from Atochem without sputtered metal and the ferric chloride etched film both served as control specimens as there was no statistically significant difference between them. Thus, it appears that the ferric chloride solution does not significantly influence the bond strength. Plasma pretreatments used in the peel strength

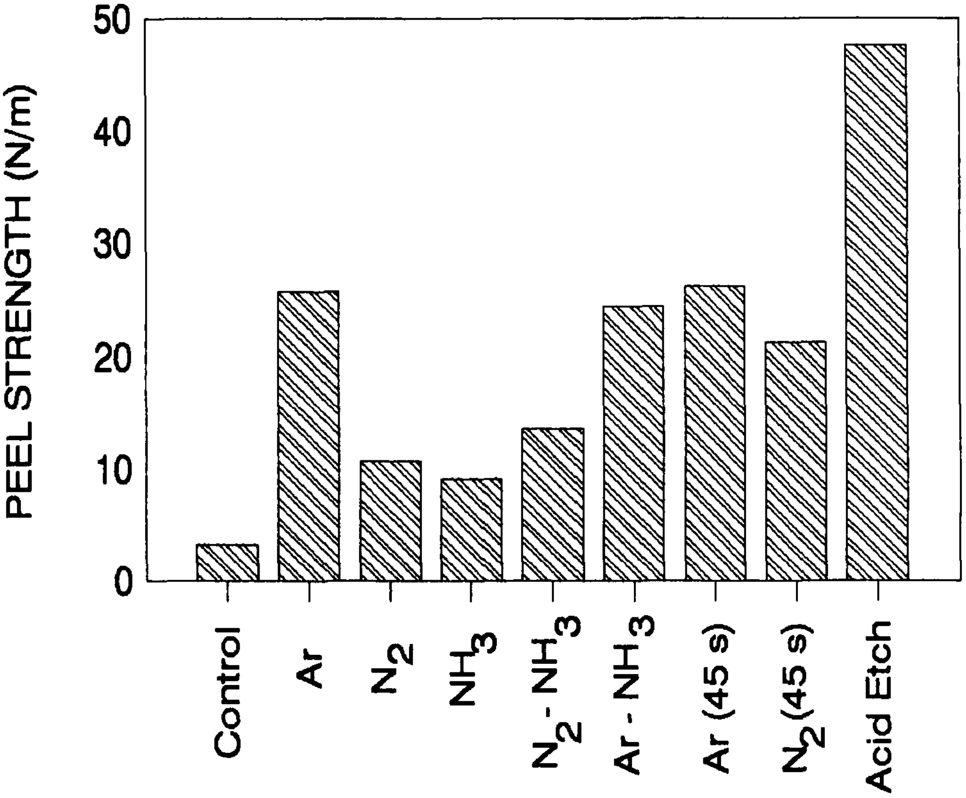

FIGURE 5 180° peel strengths for various pretreatments.

study included argon, nitrogen, ammonia, nitrogen followed by ammonia, and argon followed by ammonia pretreatments. Unless otherwise noted, each plasma pretreatment lasted two minutes (with the two double pretreatments lasting a total of four minutes). Specimens etched with the 80% Brite Dip solution for one minute were also tested.

All plasma pretreatments more than doubled the peel strength when compared with the control specimens. Even with the incorporation of nitrogen (suspected to be present in amine groups) onto the surface of the PVF_2, the ammonia plasma was the least effective. Nitrogen-treated film, although resulting in the best surface wetting, did not improve bonding as much as argon plasma. Argon, whether followed by an ammonia treatment or not, improved bonding the most with a 750% increase in peel strength. The 45-second nitrogen treatment doubled the peel strength over the two-minute nitrogen exposure, but was still weaker than the bond to the argon treated film. The doubling of the peel strength does, however, support the belief that nitrogen-treated film is over-exposed after 45 seconds, and that this over-exposure results in a weaker PVF_2 film surface.

Two more general observations concerning plasma exposed film should also be made. Firstly, employing a second pretreatment with ammonia plasma made no statistically significant difference. Secondly, the peel strengths of plasma exposed film appear to plateau at 26 N/m. It could be speculated that this peel strength represents the inherent strength of the PVF_2, were it not for the acid etch results.

The film etched with the diluted Brite Dip acid mixture had a peel strength of 47.6 N/m. This represents a 12-fold increase in peel strength over the untreated film. Thus, from a peel strength standpoint, the Brite Dip acid etch results in the best bond to the PVF_2 surface. Since the peel strength of the acid etched PVF_2 is significantly greater than the plateau reached by plasma pretreatments, it could be concluded that all of the tested plasma pretreatments weakened the top surface of the PVF_2 to some extent.

Results from the failure loci study of the peel specimens are shown in Tables IV and V. On the PVF_2 surface with no pretreatment, it appears that there is a weak layer of carbon- and oxygen-containing materials which remains adhered to the epoxy surface after failure. This is also a possibility, to a smaller extent, on the ammonia treated and the argon followed by ammonia treated specimens. However, the fluorine content on both surfaces indicates mainly a cohesive failure within the PVF_2. In all other specimens, nitrogen treated, argon treated, and acid etched, failure is clearly cohesive within the PVF_2.

Another possibility exists which would also explain both the peel strength data and the failure loci. As mentioned previously, the cohesive strength of PTFE is relatively low. If PVF_2 exhibits the same low cohesive strength, it may be that the plasma treatments do not actually weaken the film; they simply do not strengthen the surface regions. The acid etch, on the other hand, may actually strengthen the film surface by crosslinking the polymer chains or by some other mechanism, resulting in stronger bonds. This would also explain the apparent plateau in peel strength exhibited by plasma treated films.

The measured increase in peel strength of pretreated samples compared with control samples may be due to dehydrofluorination of the PVF_2 at the film surface.

TABLE IV
Elemental concentrations determined by XPS analysis of failed peel surfaces of plasma pretreated PVF_2

Pretreat	Surface	C%	O%	N%	F%
None	PVF_2	53.6	3.0	0.4	43.0
	epoxy	66.0	14.4	2.7	16.9
Nitrogen	PVF_2	50.6	0.3	0.0	49.1
	epoxy	50.9	0.9	0.0	48.2
Argon	PVF_2	50.7	0.5	0.0	48.8
	epoxy	60.6	3.9	0.3	35.2
Ammonia	PVF_2	53.3	2.0	0.6	44.0
	epoxy	53.5	1.2	0.3	45.0
Argon/Ammonia	PVF_2	50.6	1.1	0.4	47.9
	epoxy	56.8	4.4	0.3	38.6
Nitrogen 45 sec	PVF_2	58.2	13.9	0.2	27.6
	epoxy	59.0	13.8	0.4	26.7
Argon 45 sec	PVF_2	50.9	0.7	0.0	48.4
	epoxy	50.7	0.7	0.1	48.4
Acid Etch	PVF_2	51.0	0.4	0.0	48.6
	epoxy	51.2	0.5	0.0	48.3

Although the only experimental support for this conjecture is in the decrease in fluorine level in the 45-second nitrogen treatment, such a reaction has been postulated by Inagaki, Tasaka, and Kawai.[9] They proposed such a reaction in PTFE exposed to ammonia plasma and suggested that such reactions would be accelerated by substitution of hydrogen along the carbon backbone. PVF_2, of course, has hydrogen substituents along the backbone. Dehydrofluorination could result in double-bonded carbon which can be a reactive site for the epoxy adhesive. Any reactions across the bond interface would tend to increase strength.

TABLE V
Concentration ratios from XPS analysis and average failure planes of failed peel specimens

Pretreatment	Surface	O/F	N/F	C/F	Failure Plane
Control (none)	PVF_2	0.070	0.009	1.2	Interface
	epoxy	0.85	0.16	3.9	
Nitrogen Plasma 2 min	PVF_2	0.006	—	1.0	PVF_2
	epoxy	0.018	—	1.0	
Argon Plasma 2 min	PVF_2	0.010	—	1.0	PVF_2 with some epoxy
	epoxy	0.11	0.008	1.7	
Ammonia Plasma 2 min	PVF_2	0.045	0.014	1.2	PVF_2 with some epoxy
	epoxy	0.027	0.007	1.2	
Argon/Ammonia Plasma	PVF_2	0.022	0.008	1.0	PVF_2 with some epoxy
	epoxy	0.11	0.007	1.5	
Nitrogen Plasma 45 sec	PVF_2	0.50	0.007	2.1	PVF_2 with some epoxy
	epoxy	0.52	0.014	2.2	
Argon Plasma 45 sec	PVF_2	0.014	—	1.0	PVF_2
	epoxy	0.014	0.002	1.0	
Acid Etch	PVF_2	0.008	—	1.0	PVF_2
	epoxy	0.010	—	1.0	

The results for the TDCB tests were as follows. The untreated film specimen propagated at 14 N, while the critical force for the argon-plasma-exposed imbedded film specimen was 191 N. As with the 180° peel specimen, the acid etched film gave the strongest bond with a critical force of 252 N which represents a strain energy release rate of 378 N/m. In the area without the imbedded film, propagation occurred at 291 N ($G_{Ic} = 437$ N/m). Thus, by exposing the PVF_2 film to an 80% solution of Brite Dip for one minute, imbedding the film into the bondline reduces the joint strength by only 13.5%. A representative graph of the TDCB test data is shown in Figure 6.

As previously stated, piezoelectric sensitivities of the pretreated films were also measured and compared with those of untreated film. The piezoelectric sensitivities were: 1.4 mV/psi for the control specimen, 0.16 mV/psi for the argon plasma treated specimen, and 1.5 mV/psi for the acid etched specimen. These sensitivity values correspond to d_{33} values (through-the-thickness piezoelectric strain constants) of -27, -3 and -29 $C/m^2/Pa$ for the control, plasma treated and acid etched specimens, respectively. The control and acid etched specimens showed fairly good agreement with the published value of d_{33} (-33 $C/m^2/Pa$) for the KYNAR® film, as found in the Pennwalt KYNAR® Piezo Film Technical Manual.[14] Clearly, while the argon plasma does improve the wettability and bondability of the PVF_2 surface, it also largely destroys the piezoelectric properties of the film.

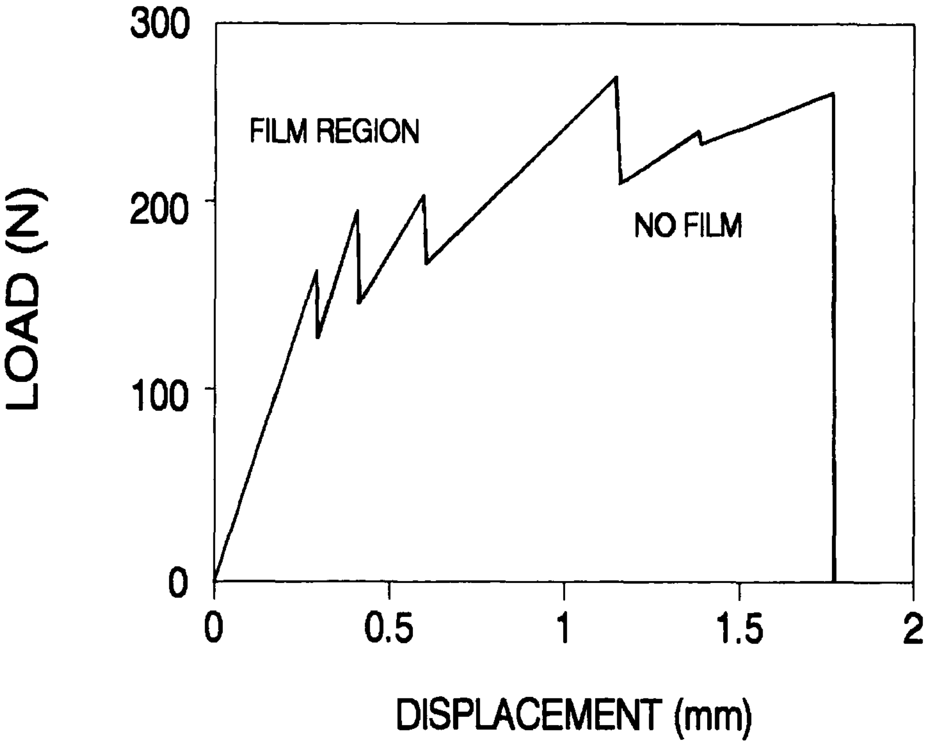

FIGURE 6 Load-displacement curve for argon plasma pretreated film (1 min) imbedded through the half bond length of a tapered double cantilever beam specimen.

Thus, this plasma pretreatment should be limited to unpoled film. Conversely, the Brite Dip acid etch produces even better bond strengths without the loss of piezoelectric properties.

CONCLUSIONS

In order to improve surface wettability and bonding to piezoelectric poly(vinylidene fluoride) (PVF_2), plasma and acid etch pretreatments were employed on the film surfaces. Oxygen, nitrogen, argon, and ammonia plasmas and an 80% Brite Dip solution were used. Contact angle measurements and XPS surface analyses were performed on pretreated surfaces in order to understand changes in the surface energetics and in the surface chemistry. In order to assess improvements in bonding to the pretreated surfaces, 180° peel and tapered double cantilever beam (TDCB) specimens were employed. Piezoelectric sensitivity of the film was also tested before and after various pretreatments.

Oxygen plasma was found to be too aggressive for piezoelectric sensor applications, but could possibly be used effectively on the unmetallized film. Argon and argon followed by ammonia plasma pretreatments produced the best peel strengths of the plasma treated film, with peel strengths being between 24 and 27 N/m. The acid etched film provided a peel strength of 48 N/m. These peel strengths represent substantial increases over the untreated film which exhibited a peel strength of only 4 N/m. The results were even more contrasting in the TDCB specimen. While a strain energy release rate of 21 N/m was observed in the untreated film, argon plasma and acid etching produced strain energy release rates of 286 and 378 N/m, respectively. These strain energy release rates compare well with TDCB specimens without imbedded film which were tested under the same conditions, yielding a value of 437 N/m.

While the argon plasma pretreatment reduced the piezoelectric sensitivity of the film by 90%, the acid etched film showed no piezoelectric reduction. Thus, an acid etch, using an 80% solution of Brite Dip, is recommended as the preferred pretreatment for *in situ* stress sensor applications.

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References

1. D. A. Dillard, G. L. Anderson and D. D. Davis, Jr., *J. Adhesion,* **29,** 245 (1989).
2. G. L. Anderson, A. R. Raheem, R. C. Robertson, A. Elshabini-Riad and D. A. Dillard, *Experimental Mechanics,* to be published.

3. E. M. Liston, *J. Adhesion*, **30,** 199 (1989).
4. H. Yasuda, H. C. March, E. S. Brandt and C. N. Reilley, *J. Polymer Science, Polymer Chemistry Ed.*, **15,** 991 (1977).
5. D. T. Clark and A. Dilks, in *Characterization of Metal and Polymer Surfaces,* Vol. 2, L. H. Lee, Ed. (Academic Press, New York, 1977).
6. J. R. Hollahan, B. B. Stafford, R. D. Falb, and S. T. Payne, *J. Applied Polymer Science,* **13,** 807 (1969).
7. Y. Momose, M. Noguchi and S. Okazaki, *Nuclear Instruments and Methods in Physics Research,* **B39,** 805 (1989).
8. A. J. Kinloch, *Adhesion and Adhesives* (Chapman and Hall, New York, 1987).
9. N. Inagaki, S. Tasaka and H. Kawai, *J. Adhesion Science and Technology,* **8,** 637 (1989).
10. T. L. St. Clair, in *Polyimides,* K. L. Mittal, Ed. (Plenum Press, New York, 1985).
11. E. J. Ripling, S. Mostovoy and R. L. Patrick, *ASTM STP 360* (1963).
12. S. Mostovoy and E. J. Ripling, *J. Applied Polymer Science,* **10,** 1351 (1966).
13. R. A. Engelman and H. K. Yasuda, *J. Applied Polymer Science: Applied Polymer Symposia,* **46,** 439 (1990).
14. Anonymous, *KYNAR® Piezo Film Technical Manual,* Pennwalt Corporation, 1987.