THE DEVELOPMENT OF POLY(VINYLDENE FLUORIDE)
PIEZOELECTRIC SENSORS FOR MEASURING
PEEL STRESSES IN ADHESIVE JOINTS

by

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THE DEVELOPMENT OF
POLY(VINYLDENE FLUORIDE) PIEZOELECTRIC SENSORS
FOR MEASURING BOND-NORMAL STRESSES
IN ADHESIVE JOINTS

by

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(ABSTRACT)

Although bond-normal stresses have been shown to be responsible for the failure of most laboratory adhesive joint geometries, the measurement of these stresses has been accomplished only through the use of very sophisticated optical techniques. In order to develop a more versatile measurement technique, poly(vinylidene fluoride) film was used to develop piezoelectric stress sensors. The sensitivities of the film to normal stresses in the three principal material directions of the orthotropic film were accurately measured using a charge amplifier and a storage oscilloscope. These measured sensitivities comprised the calibration constants of the film.

In order to reduce the detrimental effect on bond strength caused by embedding the low surface energy film into adhesive bondlines, surface treatment methods were investigated using contact angle studies, XPS analysis and 180° peel and tapered double cantilever beam adhesion specimens. An acid etch using a mixture of acetic,
phosphoric and nitric acids was found to greatly improve the bond strengths to an epoxy adhesive without reducing the piezoelectric activity of the film.

The bond-normal stresses in both the elastomeric butt joint and the single lap shear joint were measured using the developed stress sensors. Comparison of the measured stresses with calculated values obtained from closed-form analytical solutions and finite element analysis for the stresses was excellent.

The piezoelectric sensors do have several important limitations. The piezoelectric activity of the film is lost at temperatures above 100°C (210°F). Also, the sensors are only sensitive to dynamic loads. Nonetheless, the sensors provide an accurate means of measuring peel stresses in many adhesive joints of practical interest.
ACKNOWLEDGMENTS

In addition to the acknowledgments accompanying the various individual sections of this dissertation, the author wishes to express his appreciation to all those who have contributed to his studies at Virginia Tech and helped him in his research efforts.

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The assistance of Danny L. Reed in fabricating many of the adherends and substrates and explaining the use of the testing equipment is gratefully acknowledged.

The author is also thankful for the support of management in the R&D Laboratory and Advanced Technology Division of Thiokol Corporation, specifically Larry W. Poulter, Ben A. Lloyd, Grant Thompson and Robert K. Lund.
None of this effort would have been possible without the support and encouragement of my wife, Veline. She is a special lady without compare.

Finally, this dissertation is dedicated to Dr. Garron P. Anderson whose enthusiasm for the field of Mechanics of Adhesive Bonds directed my professional life. His advice and understanding are sorely missed.
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SECTION 1. INTRODUCTION

This dissertation is a compilation of three journal articles. Section 2 contains the first which was published as a note in both The Journal of Adhesion and the book The Science and Technology of Adhesive Bonding: Proceedings of the 35th Sagamore Army Materials Research Conference and was entitled "A Preliminary Study of the Use of KYNAR® Piezoelectric Film to Measure Peel Stresses in Adhesive Joints". The manuscript discussed the underlying concept and preliminary studies. Some of the hypotheses set forth therein were later discounted. Where this is the case, a short explanation of later findings is given in brackets. Sections A through C were written by Dr. David A. Dillard, and Figures 3 and 4 depict data obtained by D. Dale Davis as part of his senior project (Department of Engineering Science and Mechanics, Virginia Polytechnic Institute and State University, 1987) under the direction of Dr. Dillard.

Section 3, entitled "Improving Bonding to Piezoelectric Poly(vinylidene fluoride) for Sensor Applications", is currently being published in The Journal of Adhesion. This section discusses efforts to improve bonding to the sensor material in order to reduce the bond strength loss which originally accompanied embedment of the film.

In Section 5, the research efforts are summarized. The summary includes a short discussion of advantages and limitations of the sensors and suggested use and future efforts.

The appendices include discussions of the theoretical shear stress insensitivity of the film and measurements of the film shear sensitivity, in-plane piezoelectric sensitivity measurements, the measurement of voltage signal contribution from electrically coupled sensors, data reduction methodology, a parametric study performed to understand the effect of the embedded film on the surrounding stress field using finite element analysis and the theory of piezoelectric coefficients.

The use of the term "bond-normal stresses" in the text is an effort to group peel, cleavage and tensile stresses. In fracture mechanics, mode I parameters are used for all three types of stress. It is the author's opinion that such a grouping is
intuitively and technically correct, because the significant difference between the three
is that of stress concentration. The grouping in fracture mechanics should be correct
in continuum mechanics, also. The grouping makes particular sense with regard to the
developed sensors which are sensitive to all three types of bond-normal stresses.
SECTION 2.

Title: A PRELIMINARY STUDY OF THE USE OF KYNAR® PIEZOELECTRIC FILM TO MEASURE PEEL STRESSES IN ADHESIVE JOINTS

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G. L. Anderson, Graduate Research Assistant  
D. D. Davis, Jr., Undergraduate Student

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and

The Science and Technology of Adhesive Bonding:  
Proceedings of the 35th Sagamore Army Materials Research Conference, Eds. L. H. Sharpe and S. E. Wentworth  
Watertown, MA, 1990, pp. 245-255

Presented at: The 35th Army Sagamore Conference  
Manchester, New Hampshire  
June 1988
A. ABSTRACT

An experimental technique to measure peel stresses within adhesive joints is discussed. KYNAR® piezoelectric film is etched to create multiple discrete sensing points within the bond area. Preliminary calibration results for the film and results from bonded joints are presented. Specimens tested include single lap, double lap, and butt joints. An assessment of the technique for more widespread use in adhesive joint testing is given.

B. INTRODUCTION

A variety of test techniques have been developed to test the performance of adhesives bonded in situ within joints. Most of these techniques measure strength, fracture toughness, or adhesive modulus of the bonded joint. Techniques to measure actual stress or strain values within a bonded joint are quite few in number. The Krieger gage\(^1\) is able to measure the average shear displacement along a 12.5 mm gage length of a thick adherend joint. It has been used primarily to measure in situ shear moduli of adhesives. Brinson and his colleagues\(^2\) proposed bonding strain gages within adhesive joints to measure strains within the adhesive. Unfortunately, these gages are only sensitive to the lateral strains and not shear or peel strains. Because
the lateral strains are dominated by the behavior of the adherends rather than the adhesive, the information which can be gained is incomplete.

Other useful approaches for determining adhesive deformation fields are high precision optical techniques. Post and his colleagues\textsuperscript{3,4} have applied high frequency cross gratings to the edges of lap joints and measured displacements in two perpendicular directions with Moiré interferometry. From these deformation fields, they could compute strain fields on the edge of the entire joint. Liechti, et al.\textsuperscript{4,7} have employed classical interferometric procedures to measure the opening mode displacements for debonds along an interface between two materials. In this approach the bond is viewed from a position perpendicular to the bond plane. The technique has been applied to several material systems to determine crack opening displacements and strain energy release rates. Knauss\textsuperscript{8} has used a similar technique and carefully analyzed the entire outer surface displacement of the adherend in an attempt to measure \textit{in situ} stress-strain relations throughout the rupture process. Although these optical techniques can provide a great deal of information about adhesive joint displacements, their nature restricts them to laboratory environments.

In an effort to develop a technique which is not limited to optical isolation tables, KYNAR\textsuperscript{®} piezoelectric film, manufactured and courteously supplied by the Pennwalt Corporation, is currently under evaluation. In current embodiment, the
The piezoelectric film is sensitive to changes in load and is especially applicable to cyclic, impact, or other dynamic loading situations. The manufacturer claims that the film has a useful frequency range of 0.005 Hz. to the order of Giga Hz.\(^1\). This dynamic nature implies that the utility for measuring residual stresses would be very limited. Nonetheless, the technique has shown considerable potential for measuring mechanically induced peel stresses. Because no other technique with such versatility currently exists, this technique offers the potential to fill a portion of the significant void which now exists in experimental adhesive joint evaluation. The following results are preliminary, but do demonstrate the potential for the technique.
C. BACKGROUND AND DEVELOPMENT OF THE PEEL STRESS SENSOR

KYMAR® piezoelectric film consists of a poly(vinylidene fluoride) (PVF₂) polymer which has been uniaxially stretched and then poled through the film thickness in an extremely high electrical field at elevated temperatures to exhibit significantly greater piezoelectric properties than are obtainable with other polymers¹¹. A very thin layer of metallization is deposited on each side of the film to provide a conductive path. The film is commercially available from the Pennwalt Corporation in a variety of thicknesses from 9 to 800 µm and with a variety of metallizations. When subjected to a normal strain in any of the three principal directions, an open circuit voltage is created between the two metallizations. Theoretical considerations reveal that the films should not be sensitive to shear deformations¹² (see Appendix A). By attaching leads to the film and then subjecting the film to a changing load, a relatively large output voltage develops across the leads. For the 28µm film, for example, a 1 MPa stress normal to the film should produce an open circuit voltage of 9.5V¹¹.

KYMAR® piezoelectric film has been widely used in a variety of applications. A summary of many of these applications and patents is presented in Ref. 11. The material may be used as either a sensing unit or as an electromotional device. Of special note is an acoustic emission study by Stiffler and Henneke¹³ where they used different backing configurations to tailor the sensitivity of the film to the type of wave
they were trying to measure, thereby demonstrating some of the versatility of the film. The most relevant use of the piezoelectric film to our discussion was a study by Chou and Ekstrom\textsuperscript{14} in which they utilized KYNAR\textsuperscript{®} strips to measure contact pressures between laminated plates. By recording data during unloading steps, they were able to obtain good agreement with theory and pressure probes. Their successful results have helped provide the impetus for this current study.

One especially interesting feature of the KYNAR\textsuperscript{®} peel stress sensor is that it can be calibrated to be a "stress gage" rather than a "strain gage". This is especially advantageous for the highly constrained conditions imposed on the adhesive by the adherends which tend to significantly limit the strains. The film is quite resistant to moisture and other chemicals. In fact, the polymer is used as a sealant for corrosion protection in some applications. This suggests that the film should be quite durable for certain applications, although the long term integrity of the metallization layers and the film-metallization bonds has not been determined.

One problem with the film is that the PVF\textsubscript{2} loses its piezoelectric properties when exposed to high temperatures. The film cannot be used above 100\textdegree C, and exhibits a time dependent loss of properties at temperatures as low as 60\textdegree C\textsuperscript{11}. This temperature effect is a serious limitation to widespread use of the sensor in adhesive
joints and composite materials, because it cannot be used with high temperature cure adhesives. PVF$_2$ has a glass transition temperature of -40°C.

The volume resistivity of the polymer is quite high (15 TΩ·m), so even in the very thin films, the resistance to electron flow which discharges the metallizations is normally much higher than the impedance of ordinary instrumentation. The capacitance of the film is not negligible, and must be taken into consideration when designing any electrical circuitry for measuring the created voltage$^{11}$.

Piezoelectric constants are third order tensors which relate stress or strain, which are second order tensors, to the electric field or electric displacement which are first order tensors. For our purposes, we will express the piezoelectric constants in contracted notation with the first subscript denoting the orientation of the electric field, and the second subscript taking on values of 1 to 6 to reflect the components of the symmetric stress tensor$^{14,15}$. The values of the piezoelectric constants are given in Table 1$^{10}$. As can be seen from the table, the sensitivity in the 1 and 3 directions are similar, but the sensitivity in the 2 direction is about one order of magnitude less.

Since the electrical output of the film is

$$V = t \ g_{3i} \ \sigma_i$$
Table I. Piezoelectric Constants of KYNAR® Film\(^1\).

<table>
<thead>
<tr>
<th>Patsy Strain Constant</th>
<th>(d_{31})</th>
<th>(23 \times 10^{-12})</th>
<th>((m/m)/(V/m)) or ((C/m^2)/(N/m^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(d_{32})</td>
<td>(3 \times 10^{-12})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(d_{33})</td>
<td>(-33 \times 10^{-12})</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Patsy Stress Constant</th>
<th>(g_{31})</th>
<th>(216 \times 10^{-3})</th>
<th>((V/m)/(N/m^2)) or ((m/m)/(C/m^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g_{32})</td>
<td>(19 \times 10^{-3})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(g_{33})</td>
<td>(-339 \times 10^{-3})</td>
<td></td>
</tr>
</tbody>
</table>

\((d_{34} = d_{35} = d_{36} = g_{34} = g_{35} = g_{36} = 0)\)
where $V$ is the generated open circuit voltage, $t$ is the film thickness, $g$ is the piezoelectric stress constant and $\sigma$ is the applied stress (indicial summation notation is assumed), the output voltage is the sum of the contributions from the normal stresses in the three principal directions. Because the compliance of the film is similar to that of typical adhesive layers and because it is very thin, it adds little perturbation to the surrounding lateral strain field. For adhesive joints consisting of adherends which are relatively stiff compared to the adhesive, the lateral strains in the adhesive are essentially the same as those in the adherends. If these strains can be estimated, it is possible to assess the errors which would be anticipated due to the in-plane deformations, providing fully characterized elastic and piezoelectric properties are available. The available data do not seem complete at this time, however, suggesting the need for more calibration studies (see Appendix B).

To minimize the film’s sensitivity to stresses or strains in the in-plane directions, one should orient the film so that the 2-direction is parallel to the largest anticipated strains. For example, for the case of single and double lap joints, the film is placed with the 2-direction along the loading axis. Because the piezoelectric sensitivity in the 2-direction is an order of magnitude less than the sensitivity in the 1- and 3-directions, the adherend strains will have little effect on the output voltage from the sensor. For butt joints with relatively rigid adherends, the strain in the plane of
the film is negligible and the output voltage may be isolated from any in-plane effects by properly calibrating the material for mounting on a rigid substrate.

One advantage of the piezoelectric film technique is that it is an embedded technique rather than an edge technique such as Moiré. This permits one to measure peel stresses over any small discrete region within the adhesive layer. This can be achieved by properly etching the film to make the film sensitive to a certain region. The output voltage is only sensitive to the average dynamic stress level over the region of the film where both metallizations are intact. By etching away one or both metallizations, the region does not respond to the piezoelectric input. Using multiple leads and sampling points, a stress sensor capable of measuring peel stresses at numerous discrete locations is possible.

While etching is easily performed by using standard circuit board etchant kits, another technique being considered for making more refined grids is photolithographic pattern transfer and etching. At present this method has not yet been successful. In order to activate the chemical photoresist, an ultraviolet light is used to expose the coated film. Due to the thinness of the film metallization surface, the light passes through the side facing the light source and exposes the back side of the film as well. Thus, the same pattern would be generated on both sides after etching. Or in our case where both sides of the film are eventually subjected to the light, only the overlap
locations would survive the etching process. If a photolithographic technique is successful, the peel stress sensor could conceivably be produced on the microscopic scale. Although the sensors discussed herein were at least $10^{-6}$ m$^2$ in area, the manufacturer reports using sensing areas as small as $10^{-12}$ m$^2$ in area. These dimensions could allow one to measure the order of singularity at bond terminations.

D. EXPERIMENTAL RESULTS

Our first multi-point sensors were made with nine sensitive regions for insertion in lap joints with a 25.4 mm square overlap. The original sensor configuration is shown in Fig. 1a. It was thought that by connecting the readout device to the two leads which intersect at the desired location, the peel stresses could be measured. The signals obtained were found to be in error because the other sensitive regions were contributing to the output signal. To avoid this type of contribution, it is necessary that each stress sensor be electrically isolated from all other stress sensors. Figure 1b schematically illustrates the improved configuration. Care should be taken in the design of the sensors to electrically isolate the sensors. [Later testing demonstrated that the sensor illustrated in Fig. 1b is not properly designed. Both sensor leads must be electrically isolated. Further discussion is found in Section 3 and Appendix C.]
Figure 1. Schematic of nine point sensing grid
a) with parasitic capacitance, b) without parasitic capacitance.
The results reported herein were obtained by connecting a Tektronix Model 5113 dual beam storage oscilloscope to the output leads. Because the impedance of the module is only 1 MΩ, the decay times were quite short. Nonetheless, the outputs were very repeatable and calibration revealed quite linear output vs. input traces. Improved design will call for a higher impedance instrument such as a specially designed op amp or FET circuit or a charge amplifier, although high impedance measuring devices can be more noise sensitive and may reduce the magnitude of the output signal. The relatively low impedance of our instrumentation explains the relatively large difference from the calibration curves and the tabulated piezoelectric constants. At this time, we have estimated the output by visual inspection of the oscilloscope trace.

The first experiment was employed to test both the linearity of the applied dynamic load/voltage output relationship and the effect of metallization overlap area on the voltage output. Two film sizes, 89 mm x 89 mm and 89 mm x 6.4 mm, were placed between two steel plates of dimensions, 89 mm x 89 mm x 12.7, and loaded in an axial MTS testing machine using compression-compression square-wave cyclic loading. A piece of felt was placed on each film metallization surface in order to insulate it from contact with the steel slabs and provide a uniform stress field. The cyclic tests were performed at a minimum load of 20 lbs. and a maximum load varying from 40 to 120 lbs. in 10 lb. increments. The results are shown graphically in
Figure 2. Comparison of output from two film sizes under square wave loading.
Fig. 2. From these results, one can conclude that a linear relationship exists between the applied dynamic force and the output voltage, and, at least in square wave loading, the output voltage is independent of the area of metallization overlap. [When using a charge amplifier circuit, the measured output voltage becomes directly proportional to the area of the metallization overlap.]

The film was then used to determine the peel stress variations in single and double lap joints. Grids similar to those shown in Fig. 1b were etched in the film, and the film was bonded into lap joints made from 6061 aluminum adherends of dimensions 101.6 mm x 25.4 mm x 3.18 mm. Care was taken to assure that the less sensitive two-direction was oriented along the loading axis in order to lessen the effect of in-plane strains on the output voltage. The adhesive used was a commercially available room-temperature-cure two-part epoxy. Figures 3 and 4 graphically demonstrate the obtained results. In both cases, the results give a fair representation of the known peel stress trends.

The normal stress distribution in an elastomeric butt joint was also obtained using KYNAR® film stress sensors. A circular elastomeric disk of radius 3.81 cm was bonded between two plexiglass adherends. An etched film was bonded into one of the bondlines. Due to the axisymmetry of the specimen, a simple grid was employed consisting of a radial metallization strip on one side of the film and six
Figure 3. Single lap shear joint results from 1.03 MPa stress amplitude, a) 3-D point graph, b) 3-D surface graph, c) location of stress profile.
Figure 4. Double lap shear joint results from 1.38 MPa stress amplitude.

a) 3-D point graph, b) 3-D surface graph, c) location of stress profile.
strips perpendicular to the first on the opposite side of the film. The six perpendicular strips led from the radial strip beyond the bond of the specimen. This resulted in six stress sensitive regions at differing radial positions. The elastomeric butt joint was chosen due to its known parabolic normal stress distribution. The joint was loaded in compression using a sinusoidal wave input of 20 Hertz, average mean stresses of 0.487 Mpa and 0.731 Mpa, and average stress amplitudes, ranging from 0.292 Mpa to 0.536 Mpa. The data for 0.731 MPa average stress appears in Fig. 5. Note the parabolic stress variation which is consistent with theory.

In order to correlate the voltage outputs to dynamic stress amplitude, it was necessary to calibrate the piezoelectric film. Earlier efforts employing the same experimental method as was used to test dynamic stress/voltage linearity and overlap area dependence showed the resulting voltages to depend not only on dynamic stress amplitude but also on the mean stress level. Since this result was contrary to tests performed by the manufacturer, it was assumed that either the felt used to insulate the film metallization from the steel platens was acting as a buffer to dampen the dynamic load or the platen alignment was not exact. These two possible error sources were overcome by bonding the film sensor between circular steel platens, thereby making a tensile butt joint. In order to more completely electrically isolate the sensor from the steel platens, 19 mm thick Plexiglas spacers were bonded between the steel platens and the sensor on both sides of the sensor. The active sensor area was small in
Figure 5. Data from elastomeric butt joint subjected to 20 Hz sine-wave loading at a mean stress of 0.731 MPa.

20 Hz, 0.731 MPa mean stress
28 um Cu/Ag KYNAR film

Voltage Output (mV)

Normalized Radial Position (r/R)

stress amplitude

0.292 MPa
0.341 MPa
0.390 MPa
0.439 MPa
0.487 MPa
0.536 MPa
Figure 6. Comparison of calibration data at 10, 20 and 30 Hz sinusoidal loading.
comparison to the platen diameter, and was centered over the platen cross-section. By performing the bonding operation within the MTS axial testing device, proper alignment was guaranteed. Since the epoxy used has a Poisson’s ratio 0.34, the stress at the center of the bond was very close to the average stress\(^9\). The film was then calibrated in tension and compression using sinusoidal wave loading at 10, 20, and 30 Hertz. Mean stresses of 0.139, 0.278, 0.417, and 0.556 MPa were used with the dynamic stress amplitude varying between 0.083 and 0.5 MPa in 0.028 MPa increments. Calibration curves for the three frequencies are shown in Fig. 6. It is observed that throughout the entire range of mean stresses from compressive through tensile no mean stress effect is present. The scatter in the data is caused by the low impedance of the instrumentation. The low impedance allows the charges induced on the sensor metallization to diminish as they are generated. Thus, the measured voltages at the lower frequencies are less than those measured at the higher frequencies.

Using the calibration performed, the experimental elastomeric butt joint data were compared to theoretical predictions. It was found that the experimental data were nearly two times larger than the predicted values. A probable source of this difference is due to the use of metallic platens in the calibration procedure. Since the bond thickness between the steel platen and the film metallization was small, parasitic capacitance between the film metallization and the platen could be drawing off a
portion of the generated voltage, an effect similar to the initial crisscrossing grids. The use of glass platens for calibration should eliminate this source of error. [Further testing showed the difference to be due to in-plane stresses which were significantly greater in the calibration specimen due to the Plexiglas spacers. In-plane stresses add to the sensor voltage output due to the in-plane sensitivity of the film and the specimen geometry.]

In an effort to assess the effect of the embedded film on joint strength, tests were performed using single lap shear joints to measure the difference in joint strength due to the embedding of the piezoelectric film. Four specimens containing the film and four specimens without the film were loaded to failure in the MTS machine. The adherends of the specimens were abraded slightly with 340 grit sandpaper. The film was not pretreated physically or chemically due to the delicate nature of the metallization surface. The average bond strengths, with the respective standard deviations in parentheses, for the two sample types were: 2.53 MPa (0.35) for the bonds without film embedded and 1.81 MPa (0.32) for those with film. All failures for the samples without the film appeared, by visual inspection, to occur interfacially between the adhesive and the adherend. All failures in samples containing the film appeared to occur, also determined by visual inspection, at the interface between the adhesive and the piezoelectric film. The low value for the samples without film could be improved by using an anodization surface pretreatment, but the even lower value
for the samples containing the film represent a very restrictive load limitation for embedded film adhesive joints. Testing may need to be done at quite small load levels or in compression to avoid failure at the KYNAR® film interface (see Section 2).

E. SUMMARY AND CONCLUSIONS

Peel stresses are often believed to be the most critical stresses responsible for failure of a variety of adhesive joints. Metallized poly(vinylidene fluoride) films have been etched to provide multi-point sensors which can be embedded within adhesive joints to measure these peel stresses. Preliminary data suggest that the technique may offer potential to partially fill the significant void now existing in experimental adhesive joint testing. Although the approach is a dynamic technique and does have temperature and load restrictions, it has successfully illustrated the peel stress trends expected in single and double lap joints and in tensile butt joints. Calibration studies have revealed that the output is quite linear and is independent of the mean stress level in tension and compression. Output has been measured with an oscilloscope, although improved circuitry is currently being designed to improve the decay time of the output voltage. Fairly large errors exist between calibration results and known stress fields, but the errors are believed to be caused by the existing instrumentation. This should be corrected by improved measurement capabilities. Photoresist techniques have not
yet been entirely successful, but may offer the potential to miniaturize the sensors to microscopic dimensions, thereby allowing peel stresses near steep gradients to be measured.

F. ACKNOWLEDGEMENTS

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G. REFERENCES


SECTION 3.

Title: IMPROVING BONDING TO PIEZOELECTRIC POLY(VINYLPIDENE FLUORIDE) FOR SENSOR APPLICATIONS

Authors: G. L. Anderson (Senior Engineer; Thiokol Corporation)
D. A. Dillard (Associate Professor; Virginia Tech)
J. P. Wightman (Professor; Virginia Tech)

Literature Citation: The Journal of Adhesion, in press

Presented At: 14th Annual Meeting of The Adhesion Society
Clearwater, Florida
February 1991
A. ABSTRACT

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.

B. 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.

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 PVF₂. 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 PVF₂ 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 PVF₂. 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. 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. 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 film and improved adhesion. The effects of the pretreatments on the piezoelectric properties of the film were also investigated.

C. EXPERIMENTAL

1. 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 PVF₂ surfaces during production in order to aid in the poling of the film. Film poling is a method of electrically aligning the CH₂-CF₂ 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 PVF₂ 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 and the
Table I. Summary of pretreatments. Dashes link prior common steps to following groups, e.g. all plasma-treated films were previously metallized film, etched with ferric chloride and wiped with methanol.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Etching Solution</th>
<th>Cleaning Solvent</th>
<th>Plasma Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Yes</td>
<td>Brite Dip</td>
<td>Water</td>
<td>Oxygen</td>
</tr>
<tr>
<td></td>
<td>Ferric Chloride</td>
<td>Acetone</td>
<td>Nitrogen</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Methanol/Water</td>
<td>Argon</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Methanol</td>
<td>Ammonia</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>N_2/Air</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>Ar/Ammonia</td>
</tr>
</tbody>
</table>
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 x 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.
Figure 1. Schematic diagram of Plasmod reactor vessel.
An acid etch, using Brite Dip, was also investigated as a surface chemical modification technique to increase the surface energy of the PVF₂ 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.

2. 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 MgKα (1253.6 eV) achromatic X-ray source. The source operated at 14 keV with an emission current of 20 mA. Pressure less than 2 x 10⁻⁷ torr was maintained throughout the analysis. Measurements were made at a 45° incident angle.
3. Peel Tests

In order to assess the improvement in bonding to the PVF₂ 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 PVF₂ film.

4. 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.

5. Tapered Double Cantilever Beam Tests

In order to assess any bond weakening due to embedded 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\textsuperscript{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. A schematic drawing of the TDCB specimen employed in the study is shown in Figure 2.

The embedded 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 embedded film by placing the clamp just past the initial taper.
Figure 2. Schematic of tapered double cantilever beam specimen showing clamp used during crack initiation and embedded film.
section. By embedding the film in only the first half of the joint length and testing the entire joint length, the fracture energy with and without the embedded 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 plasma treatment resulting in the highest peel strength, and the 80% Brite Dip etched films were studied. As a control, untreated films were also embedded into a TDCB bondline.

6. 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.
D. 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 metal 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 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$_2$. 
Figure 3. Water contact angle measurements on PVF$_2$ film as a function of plasma exposure time.
Ammonia and argon plasma pretreatments of the PVF<sub>2</sub> 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<sub>2</sub> surface which could create a rough micro-surface, resulting in an increased contact angle. As the PVF<sub>2</sub> 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<sub>2</sub>.

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<sub>2</sub> 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<sup>9</sup>. In order to reduce the possibility of piezoelectric loss and to minimize PVF<sub>2</sub> 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 PVF₂. 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 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 surfaces of the KYNAR® film which apparently is not completely removed
Figure 4. Summary of minimum water contact angles for all pretreatments studied. Treatment times shown in parentheses.
Table II. Elemental concentrations from XPS analysis of pretreated PVF$_2$ films.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Atomic Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>None</td>
<td>62.9</td>
</tr>
<tr>
<td>Nitrogen Plasma</td>
<td>51.4</td>
</tr>
<tr>
<td>Argon Plasma</td>
<td>52.5</td>
</tr>
<tr>
<td>Ammonia Plasma</td>
<td>63.4</td>
</tr>
<tr>
<td>Acid Etch</td>
<td>58.8</td>
</tr>
</tbody>
</table>
by the dilute ferric chloride solution. The metal content on the surface is reduced following any of the plasma treatments. 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 PVF₂ 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" PVF₂ surface. This trend is confounded, however, by the fact that plasma treatments are also expected to cause defluorination of the PVF₂⁹ 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 the pretreatment or from ammonia nitrogen incorporation during pretreatment. Nitrogen
Table III. Comparison of carbon-fluorine and nitrogen-carbon surface elemental ratios.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>C%</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>4.8</td>
<td>0.021</td>
</tr>
<tr>
<td>Nitrogen Plasma</td>
<td>1.5</td>
<td>0.027</td>
</tr>
<tr>
<td>Argon Plasma</td>
<td>2.5</td>
<td>0.021</td>
</tr>
<tr>
<td>Ammonia Plasma</td>
<td>3.1</td>
<td>0.107</td>
</tr>
<tr>
<td>Acid Etch</td>
<td>1.8</td>
<td>0.020</td>
</tr>
</tbody>
</table>
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\textsuperscript{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, \textit{et al}\textsuperscript{4}.

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\textsubscript{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 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 PVF₂, 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 PVF₂ 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 PVF₂, were it not for the acid etch results.
Figure 5. 180 degree peel strengths for various pretreatments.

Peel Strength (N/m)
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 PVF₂ surface. Since the peel strength of the acid etched PVF₂ 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 PVF₂ to some extent.

Results from the failure loci study of the peel specimens are shown in Tables IV and V. On the PVF₂ 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 PVF₂. In all other specimens, nitrogen treated, argon treated, and acid etched, failure is clearly cohesive within the PVF₂.

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 PVF₂ exhibits the same low cohesive strength, it may be that the
Table IV. Elemental concentrations determined by XPS analysis of failed peel surfaces of plasma-treated PVF$_2$.

<table>
<thead>
<tr>
<th>Pretreat</th>
<th>Surface</th>
<th>C%</th>
<th>O%</th>
<th>N%</th>
<th>F%</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>PVF$_2$</td>
<td>53.6</td>
<td>3.0</td>
<td>0.4</td>
<td>43.0</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td>66.0</td>
<td>14.4</td>
<td>2.7</td>
<td>16.9</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>PVF$_2$</td>
<td>50.6</td>
<td>0.3</td>
<td>0.0</td>
<td>49.1</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td>50.9</td>
<td>0.9</td>
<td>0.0</td>
<td>48.2</td>
</tr>
<tr>
<td>Argon</td>
<td>PVF$_2$</td>
<td>50.7</td>
<td>0.5</td>
<td>0.0</td>
<td>48.8</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td>60.6</td>
<td>3.9</td>
<td>0.3</td>
<td>35.2</td>
</tr>
<tr>
<td>Ammonia</td>
<td>PVF$_2$</td>
<td>53.3</td>
<td>2.0</td>
<td>0.6</td>
<td>44.0</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td>53.5</td>
<td>1.2</td>
<td>0.3</td>
<td>45.0</td>
</tr>
<tr>
<td>Argon/Ammonia</td>
<td>PVF$_2$</td>
<td>50.6</td>
<td>1.1</td>
<td>0.4</td>
<td>47.9</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td>56.8</td>
<td>4.4</td>
<td>0.3</td>
<td>38.6</td>
</tr>
<tr>
<td>Nitrogen 45 sec</td>
<td>PVF$_2$</td>
<td>58.2</td>
<td>13.9</td>
<td>0.2</td>
<td>27.6</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td>59.0</td>
<td>13.8</td>
<td>0.4</td>
<td>26.7</td>
</tr>
<tr>
<td>Argon 45 sec</td>
<td>PVF$_2$</td>
<td>50.9</td>
<td>0.7</td>
<td>0.0</td>
<td>48.4</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td>50.7</td>
<td>0.7</td>
<td>0.1</td>
<td>48.4</td>
</tr>
<tr>
<td>Acid Etch</td>
<td>PVF$_2$</td>
<td>51.0</td>
<td>0.4</td>
<td>0.0</td>
<td>48.6</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td>51.2</td>
<td>0.5</td>
<td>0.0</td>
<td>48.3</td>
</tr>
<tr>
<td>Pretreatment</td>
<td>Surface</td>
<td>O/F</td>
<td>N/F</td>
<td>C/F</td>
<td>Failure Plane</td>
</tr>
<tr>
<td>-------------------</td>
<td>---------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-------------------------</td>
</tr>
<tr>
<td>None</td>
<td>PVF₂</td>
<td>0.070</td>
<td>0.009</td>
<td>1.2</td>
<td>Interface</td>
</tr>
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<td>0.16</td>
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<tr>
<td>Nitrogen Plasma</td>
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<td>0.006</td>
<td>-</td>
<td>1.0</td>
<td>PVF₂</td>
</tr>
<tr>
<td>2 min</td>
<td>epoxy</td>
<td>0.018</td>
<td>-</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Argon Plasma</td>
<td>PVF₂</td>
<td>0.010</td>
<td>-</td>
<td>1.0</td>
<td>PVF₂ with some epoxy</td>
</tr>
<tr>
<td>2 min</td>
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<td>0.11</td>
<td>0.008</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Ammonia Plasma</td>
<td>PVF₂</td>
<td>0.045</td>
<td>0.014</td>
<td>1.2</td>
<td>PVF₂ with some epoxy</td>
</tr>
<tr>
<td>2 min</td>
<td>epoxy</td>
<td>0.027</td>
<td>0.007</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Argon/Ammonia</td>
<td>PVF₂</td>
<td>0.022</td>
<td>0.008</td>
<td>1.0</td>
<td>PVF₂ with some epoxy</td>
</tr>
<tr>
<td>Plasma</td>
<td>epoxy</td>
<td>0.11</td>
<td>0.007</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Nitrogen Plasma</td>
<td>PVF₂</td>
<td>0.50</td>
<td>0.007</td>
<td>2.1</td>
<td>PVF₂ with some epoxy</td>
</tr>
<tr>
<td>45 sec</td>
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<td>0.52</td>
<td>0.014</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Argon Plasma</td>
<td>PVF₂</td>
<td>0.014</td>
<td>-</td>
<td>1.0</td>
<td>PVF₂</td>
</tr>
<tr>
<td>45 sec</td>
<td>epoxy</td>
<td>0.014</td>
<td>0.002</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Acid Etch</td>
<td>PVF₂</td>
<td>0.008</td>
<td>-</td>
<td>1.0</td>
<td>PVF₂</td>
</tr>
<tr>
<td></td>
<td>epoxy</td>
<td>0.010</td>
<td>-</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>
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 PVF₂ at the film surface. 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 Kawai⁹. 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. PVF₂, 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.

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 embedded 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. The failure in the film region was at the film to adhesive interface as determined by visual inspection. In the area without the embedded film, propagation occurred at 291 N (Gk = 437 N/m) with the locus of failure cohesive within the adhesive layer. Thus, by exposing the PVF2 film to an 80% solution of Brite Dip for one minute, embedding 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. The crack extension occurred in a slip-stick behavior as observed in the sawtooth load-displacement trace. The critical loads are the peak loads in the trace. These critical loads were averaged in the embedded film region and in the region without the film in order to calculate the critical strain energy release rates.

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 d33 values (through-the-thickness piezoelectric strain constants) of -27, -3 and -29 C/m²/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 d33 (-33 C/m²/Pa) for the KYNAR® film, as found in the Pennwalt KYNAR® Piezo Film Technical Manual14.
Figure 6. Load-displacement trace for TDCB containing an argon plasma-treated film embedded in half of the bond.
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. 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.

E. 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$^\circ$ 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 embedded 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.

F. ACKNOWLEDGMENTS

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acknowledged. Francis Webster and Pascal Commerçon are appreciated for their help with the XPS work and acid etching. Joannie Chin provided the schematic drawing of the Plasmod reactor. Finally, the authors wish to acknowledge the Center for Adhesive and Sealant Science for encouraging interdisciplinary research.
G. REFERENCES


SECTION 4.

Title: THE DEVELOPMENT OF EMBEDDED PIEZOELECTRIC SENSORS TO MEASURE PEEL STRESSES IN ADHESIVE JOINTS

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Literature Citation: Experimental Mechanics, submitted

Presented At: 1990 Conference of the Society of Experimental Mechanics  
Albuquerque, NM  
June 1990
A. ABSTRACT

Although peel stresses are believed to be responsible for failure in many adhesive joint geometries, the measurement of these peel stresses has been elusive. Embedded poly(vinylidene fluoride) piezoelectric sensors were used to measure peel stresses in adhesively bonded joints. Piezoelectric KYNAR® film was etched to produce multi-point stress sensors which were bonded into adhesive joints. Calibration results and results for single lap and elastomeric butt joints are presented. The elastomeric butt joint was compared with an analytical solution for the bond-normal stresses, while the single lap joint results were compared to finite element analysis. Promising features and limitations of this technique are discussed.

B. INTRODUCTION

The importance of peel stresses in a wide variety of adhesive joints has become clear. DeVries and his colleagues\textsuperscript{1} were able to employ mode I strain energy release rates ($G_i$) to predict the bond strengths of cantilever beam, tensile button, and single and double lap shear joints. Some of the joints mentioned are loaded in a tensile mode for which a $G_i$ value would intuitively be used. The lap shear joints, however, are loaded in a shearing mode. The accurate prediction of the strength of these shear specimens employing only mode I parameters leads to the conclusion that these joints, although loaded in a shear mode, actually fail due to tensile or peel stresses which are
induced upon loading. It is also known that for most adhesives the values of $G_k$ are significantly smaller than those of $G_{tk}$, which further supports the tendency of adhesives to fail due to peel stresses.\endnote{2}

A variety of measurement techniques which test the performance of adhesively bonded joints have been developed. Most of those techniques measure the strength or some fracture mechanics parameter of the adhesive and are destructive in nature. Techniques which measure the actual stresses or strains present in a loaded joint are few in number. The Krieger gage\footnote{3} is able to measure the average shear displacement over a 12.5 mm length of a thick adherend lap shear joint and has been used primarily to measure the \textit{in situ} shear modulus of the bonding adhesive. Brinson and his associates\footnote{4} proposed bonding strain gages within adhesive joints to measure in-plane normal strains within the adhesive. Because these in-plane strains are dominated by the behavior of the adherends rather than the adhesive, the information which can be gained is incomplete.

Other useful techniques for measuring \textit{in situ} adhesive deformation fields are high-precision optical methods. Post and his co-workers\footnote{5} have applied high frequency cross gratings to the edges of lap joints and measured displacements in two perpendicular directions with Moiré interferometry. From these deformation fields it is possible to compute the stress and strain fields along the entire edge of the joint.
Liechti, et al. have employed classical interferometric procedures to measure the opening mode displacements for debonds along a bi-material interface. In this approach the bond is viewed from a position perpendicular to the bond plane. The technique has been applied to several material systems in order to determine crack opening displacements and strain energy release rates. Knauss has used a similar technique and carefully analyzed the outer surface displacement of the adherend in an attempt to measure the stress-strain behavior of the bonded system throughout the fracture event. These photomechanical techniques can provide useful information concerning the peel stresses which are of such great importance.

Techniques developed thus far are very sophisticated research methods, and are limited to laboratory conditions by their very natures. An additional limitation of the optical techniques discussed is the need to use at least one transparent adherend or substrate.

There currently exists a significant gap in the area of experimental adhesive joint testing which consists of a measurement technique which will measure peel stresses outside of laboratory environments in a nondestructive manner. In an effort to fill this void, stress sensors made from KYNAR® piezoelectric film, manufactured by Atochem North America (formerly the Pennwalt Corporation), were investigated. Although the technique has limitations, to be discussed herein, it has shown
considerable potential for measuring mechanically induced peel stresses. Because no other technique with such potential versatility is now in use, the development of this technique may partially meet the existing experimental needs.

C. DEVELOPMENT OF THE PIEZOELECTRIC STRESS SENSOR

KYNAR® piezoelectric film consists of poly(vinylidene fluoride) or PVF₂ which has been laterally stretched in one direction and then transversely poled in a high electrical field at elevated temperatures. During the stretching and poling processes, the PVF₂ is converted from the random atactic form (the α phase) to the polar isotactic form (the β phase). By cooling the film while in the electrical field, the aligned isotactic polymer chains and their dipole moments are "frozen" in place creating a material with significantly greater piezoelectric properties than are obtainable with other polymers¹². A very thin layer of metallization is vapor deposited on each side of the film to aid in the piezoelectric poling and to provide a conductive path. The film is commercially available from Atochem North America in a variety of thicknesses from 9 to 800 μm and with a variety of metallization alloys. The present work employed 52 μm, copper-nickel surfaced film.

When subjected to a normal strain in any of the three principal material directions, an open circuit voltage is created between the two metallization surfaces.
Theoretical considerations indicate that the film should be insensitive to shear stresses\textsuperscript{13}. The induced voltage diminishes with time; its time constant depends on both the film’s dielectric constant and the internal impedance of any connected circuits. This dynamic nature implies that the utility of the technique for measuring residual stresses will be limited. The technique is, however, especially applicable to cyclic or impact loading situations.

KYNAR\textsuperscript{®} piezoelectric film has been widely used in a variety of applications. A summary of many of these applications and related patents is given in Ref. 12. The material may be used as either a dynamic stress (or strain) sensing device or as an electromotional device. The most relevant use of the piezoelectric film to our research was a study by Chou and Ekstrom\textsuperscript{14} in which KYNAR\textsuperscript{®} strips were utilized to measure contact pressure between laminated plates. By recording data during unloading steps, they were able to obtain good agreement with pressure probes and theory. Their successful results provided the impetus for this current study.

The present technique consists of etching discrete stress sensors onto the metallized surface of the film, then introducing the film into the adhesive bondlines prior to cure. After the adhesive joints containing the stress sensors were cured, instrumentation leads were attached to the sensors, and the joints were cyclically
loaded. The voltages produced by the sensors were measured and converted to the stresses at the sensor locations.

The produced voltages can only be measured in the region of the film in which both metallizations remain intact. Thus by partially etching away the metallization surfaces of the film, multi-point sensors can be made. Our first multi-point sensors were made with three horizontal metallization strips intersecting three vertical strips to form a nine-point sensor. It was thought that by connecting the voltage measurement device to any two intersecting leads, the average peel stresses in the finite region of the lead overlap area could be measured. After further investigation it was found that all other sensor locations were contributing to the output as they were electrically coupled. As a result, it was found to be necessary to electrically isolate all leads (see Appendix C). Figure 1 schematically illustrates the improved configuration for a 25.4 mm square bondline.

The actual construction of multi-point sensors was performed in two ways. The simplest method was to protect the areas which were desired as sensors and sensor leads with narrow strips of adhesive border tape. The metallized film is then dipped in a bath of diluted standard circuit board etchant containing ferric chloride, and quickly and thoroughly rinsed with water.
Figure 1. Stress sensor grid made for single lap joint with 25.4 mm square bondline.
Another method which produced better line definition and could conceivably allow the miniaturization of the stress sensor grids to the order of $10^3$ mm$^2$ is the photolithographic pattern transfer technique. Although the miniaturization potential has not yet been realized, the technique was used for many of our sensor grids. The film is first cut to dimensions slightly larger than the desired stress sensor grid in order to allow handling of the film.

The piezoelectric film was thoroughly cleaned with acetone to remove any undesirable deposits, and then washed in distilled water and dried with filtered air. Two photographic films containing positives of the top and bottom sensor patterns with alignment markers, which aid in the aligning of the two patterns, were produced using a CAD computer system. The photographic films are then aligned and secured between two glass plates. Positive photoresist was spin coated on one KYNAR® film surface at a speed of 2500 rpm for 20 seconds. Afterwards, the photoresist was dried for two hours at $20^\circ$C. The other film surface was also coated with photoresist in order to protect that entire surface from the etchant. After complete drying, the film was placed between the aligned sensor patterns, and the spin coated side was exposed to ultraviolet light for seven seconds. The appropriate chemical developer was then applied to the film, and the film was washed, dried, and etched with a dilute ferric chloride solution. The photoresist was removed using acetone, and the procedure was
repeated on the other side of the film. It was necessary for the film to be properly realigned within the secured pattern plates in order to obtain well-defined sensors.

D. THEORETICAL CONSIDERATIONS

Piezoelectric constants are third-order tensors which relate stress or strain, which are second-order tensors, to the first-order tensors of electrical field intensity or electrical displacement. By employing contracted indicial notation for the stress or strain with a single index ranging from one to six, the piezoelectric constants will have only two indices\textsuperscript{15,16}. In order to understand more fully the piezoelectric constants and the constitutive relation of the film, a numerical classification of the film axes is necessary. The 1-direction of the film is the stretched in-plane direction, the 2-direction is perpendicular to the 1-direction and also in the plane of the film, and the 3-direction is in the poling direction perpendicular to the film plane. Experimental values of the piezoelectric constants are found in Ref. 12 and are shown in Table 1. As is evident from the table, the sensitivity in the 1- and 3-directions are similar, but the 2-direction sensitivity is an order of magnitude less.

The electrical output of the film is given by the following constitutive relation:

\[ V = t \cdot g_{3\alpha} \cdot \sigma_\alpha \]
Table I. Piezoelectric constants of KYNAR® film\textsuperscript{12}.

<table>
<thead>
<tr>
<th>Patsy Strain Constant</th>
<th>( d_{31} )</th>
<th>( 23 \times 10^{-12} )</th>
<th>(m/m)/(V/m) or (C/m(^2))/(N/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{32} )</td>
<td>( 3 \times 10^{-12} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( d_{33} )</td>
<td>( -33 \times 10^{-12} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Patsy Stress Constant</th>
<th>( g_{31} )</th>
<th>( 216 \times 10^{-3} )</th>
<th>(V/m)/(N/m(^2)) or (m/m)/(C/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g_{32} )</td>
<td>( 19 \times 10^{-3} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( g_{33} )</td>
<td>( -339 \times 10^{-3} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\((d_{34} = d_{35} = d_{36} = g_{34} = g_{35} = g_{36} = 0)\)
where $V$ is the generated open circuit voltage, $t$ is the film thickness, $g_{3\alpha}$ is the piezoelectric stress constant in the normal (3) direction, and $\sigma_\alpha$ is the contracted form of the applied stress. Indicial summation notation is assumed with the contracted index, $\alpha$, ranging only from 1 to 6. Due to the shear stress insensitivity of the film, constants $g_{34}$, $g_{35}$, and $g_{36}$ are equal to zero. Thus, the voltage output represents the sum of the contributions from the normal stresses in all three principal material directions. For adhesive joints consisting of adherends which are relatively stiff compared with the adhesive, the in-plane strains of the adhesive are essentially the same as those in the adherends. If these strains are estimated or measured, it then becomes possible to assess the contributions which would result due to the in-plane deformations. In cases where the strains in the plane of the film vary with orientation, the film sensors can be preferentially aligned with the 2-direction coinciding with the direction of the largest strain. By so doing, the voltage contributions of the in-plane stresses and strains will be less. This was done in tests with single lap joints in which the 2-direction of the film was oriented in the line of the loading. A constitutive relationship of similar form relating the produced voltage to the applied strains may also be employed, in which the piezoelectric strain constants, $d_{3\alpha}$, are introduced.

The present technique suffers from various limitations due to the nature of the piezoelectric stress sensors. One problem is that the PVF$_2$ film loses its piezoelectric properties when exposed to high temperatures. As a result, the film cannot be used in
piezoelectric applications above 120°C. In addition, it exhibits a time-dependent loss of properties at temperatures as low as 70°C\textsuperscript{12}. PVF\textsubscript{2} also has a melt temperature between 165° and 180°C at which point the piezoelectric properties of the film will be permanently lost\textsuperscript{17}. These temperature limitations seriously restrict the widespread use of the technique in many adhesive joints and composite materials because the film cannot be used with high temperature cure adhesives. The limitation to dynamic load inputs has been previously discussed in this paper.

Notwithstanding these limitations, there are many important advantages to the use of piezoelectric stress sensors in measuring peel stresses in adhesive joints. Although input loads must be dynamic in nature, the useful frequency range of the film spans twelve decades, from mHz to GHz.

One especially important feature of the KYNAR\textsuperscript{®} stress sensor is that it can be calibrated as a "stress gage" rather than a "strain gage". This is especially advantageous for the highly constrained conditions imposed on the adhesive layer by the adherends which tend to limit the strains significantly. Also, because the compliance of the film is similar to that of many adhesives, an adhesive may be chosen which has similar mechanical properties in order to minimize the perturbation to the strain field in the adhesive caused by embedding the sensor within the bondline. As the adhesive mechanical properties vary increasingly from those of the sensors, the
strain field in the adhesive layer will be altered. The adhesive used in this study has a modulus value of 2.0 GPa which is near that of the PVF$_2$ film, 2.3 GPa.

The film is quite resistant to moisture and other chemicals. In fact, the polymer is used as a sealant for corrosion protection in some applications$^{17}$. Although the PVF$_2$ film itself should be quite durable in most applications, the long term integrities of the metallization surfaces and the PVF$_2$-metallization bonds are questionable.

Another advantage of the piezoelectric film technique is that it is an embedded technique rather than an edge technique. Thus, the present technique permits the measurement of peel stresses over any discrete region within the adhesive layer.

E. CALIBRATION AND PRELIMINARY EXPERIMENTAL STUDIES

Preliminary studies were performed with the film in order to gain knowledge concerning the use of the piezoelectric stress sensors. Voltage measurements were made with the use of a Brüel and Kjaer Model 2635 charge amplifier. The appropriate sensor leads were connected to the charge amplifier which sent the amplified signal to a Tektronix model 5113 dual beam storage oscilloscope. The charge amplifier both amplified the induced signal, or attenuated it in regions of very
high stress, and filtered out electrical "noise" of frequency greater than 100 Hz. More complicated circuitry could be employed, such as a specially designed high impedance op amp or FET circuit which should lengthen the decay time. In the present study, however, no such complication appeared to be necessary as the output measured by the current instrumentation seems to be reliable based on the very small amount of scatter in the calibration measurements (see Figure 3).

A series of tests was undertaken to calibrate the film using our measurement instrumentation. A tensile butt joint specimen was found to be well suited for the calibration as the local normal stresses never vary more than 1 1/2 percent from the average normal stress within the inner portion of the bond up to a normalized radial position of 0.7. Bonding of the joint with a two-part epoxy adhesive was performed within the MTS testing device in order to insure proper alignment. A sheet of piezoelectric film with one stress sensor located in the center of the film was introduced into the bond prior to curing. The area of the stress sensor was small (10 mm²) compared with that of the steel platens (7130 mm²), thus stresses were measured only in a small region in the center of the calibration joints. The calibration joint is shown in Fig. 2. After curing, the joint was subjected to varying sinusoidal stress inputs in tension and compression. Care was taken to cycle the loading in a tension-tension or compression-compression manner but not in a mixed manner (tension-compression) in order to observe any difference in the sensor output between
Figure 2. Calibration specimen with Plexiglas spacers.
tensile and compressive loading. The dynamic stress input was varied between 0.08 and 0.5 MPa at frequencies of 0.25, 0.5, 1, 2, 5, 10, 20, and 30 Hz. In order to reduce the in-plane strain constraint of the steel platens, Plexiglas spacers 6.4 mm thick were inserted into the bondline of several calibration specimens. Figure 3 presents typical results for a calibration specimen at three frequencies and five different mean stresses. Linear regression analyses were performed on all calibration specimens, and linear regression slopes, calculated y intercepts, and $R^2$ values are shown in Table 2. All $R^2$ values were greater than 0.997, indicating the highly linear response of the film over the stress amplitudes tested.

Slopes obtained by linear regressions of the results from various specimens are shown in Fig. 4. These slopes represent the system sensitivity and depend on the measurement circuitry used. The lower two data sets represent tensile and compressive testing of a specimen without Plexiglas spacers, while the upper group of data represents specimens with spacers. The different slope magnitudes for the two sets of specimen indicate the influence of the in-plane normal stress sensitivity of the sensors.

In order to relate the measured sensitivities of the film and electrical circuitry employed in the current study to the published values of the piezoelectric strain constants, similar measurements were made using an electrometer. The sensitivities of
Figure 3. Typical calibration results at 10, 20 and 30 Hz at five different mean stresses.

52 μm Cu/Ni Film
Plexiglas spacers employed
3.2 mm x 3.2 mm sensor

Voltage Amplitude (mV)

Stress Amplitude (MPa)
Table II. Calculated linear regression parameters for the calibrations. Values within parentheses represent compression tests; those within parentheses represent tensile tests.

<table>
<thead>
<tr>
<th>Spacers</th>
<th>Frequency (Hz)</th>
<th>Slope (mV/MPa)</th>
<th>Y-int (mV)</th>
<th>R²</th>
</tr>
</thead>
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<tr>
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<td>101 (99)</td>
<td>1.1 (0.8)</td>
<td>1.000 (0.999)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>190 (185)</td>
<td>-0.6 (1.2)</td>
<td>0.999 (1.000)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>211 (237)</td>
<td>1.0 (1.5)</td>
<td>1.000 (1.000)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>263 (243)</td>
<td>-0.6 (-4.8)</td>
<td>1.000 (0.997)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>265 (243)</td>
<td>-1.4 (-1.6)</td>
<td>1.000 (1.000)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>258 (244)</td>
<td>-1.8 (-6.2)</td>
<td>0.999 (1.000)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>263 (243)</td>
<td>0.2 (-6.8)</td>
<td>0.997 (1.000)</td>
</tr>
</tbody>
</table>

|         | 0.5            | 101 (92)       | 0.5 (1.2)  | 1.000 (0.999) |
|         | 1              | 190 (174)      | 0.7 (1.3)  | 1.000 (1.000) |
|         | 2              | 243 (218)      | 0.2 (2.5)  | 0.999 (1.000) |
|         | 5              | 254 (240)      | 3.7 (0.4)  | 1.000 (1.000) |
|         | 10             | 258 (243)      | 0.6 (-0.2) | 1.000 (1.000) |
|         | 20             | 257 (244)      | 2.5 (-1.4) | 1.000 (1.000) |
|         | 30             | 260 (243)      | -0.5 (-0.6)| 1.000 (1.000) |

| No      | 0.25           | - (25)         | - (0.0)    | - (0.990) |
|         | 0.5            | - (60)         | - (1.1)    | - (0.999) |
|         | 1              | - (123)        | - (0.8)    | - (0.996) |
|         | 2              | - (152)        | - (4.9)    | - (0.997) |
|         | 5              | - (164)        | - (3.3)    | - (0.999) |
|         | 10             | 164 (164)      | 3.4 (1.5)  | 0.999 (0.998) |
|         | 20             | 160 (174)      | 3.8 (2.5)  | 0.999 (1.000) |
|         | 30             | 166 (177)      | 3.4 (2.1)  | 1.000 (1.000) |
Figure 4. Comparison of calibration slopes (sensor sensitivities) as a function of frequency.
the film to stresses perpendicular to the film plane with and without the Plexiglas spacers were found to be $-33 \times 10^{12}$ and $-22 \times 10^{12} \text{(C/m}^2\text{)/Pa}$, respectively. These values coincide with those published in the *KYNAR® Piezo Film Technical Manual*\textsuperscript{12} for states of uniaxial stress and uniaxial strain. The coincidence with the uniaxial strain condition is expected, since a minimum bond thickness was used in the test without the spacers and the steel is relatively rigid.

The match of the test with spacers to the published value for the uniaxial stress state was not expected. The difference in Young’s modulus between the steel and Plexiglas suggests that the radial and tangential stresses at the steel-Plexiglas interface are about 40 percent of the axial stress at the bond center\textsuperscript{20}. The ratio of thickness to diameter of each spacer (8.6) is too large to expect a significant decrease in the radial and tangential stresses at the center of the spacers where the sensor was located. The good correlation of the uniaxial strain value and the grounding of the MTS testing device would tend to eliminate from consideration any capacitance effects between the sensor and steel platens. Other possible causes for the unexpectedly good correlation with the uniaxial stress piezoelectric constant include the possibility that the published value was measured in a multi-axial stress state and batch-to-batch variation of the film. The possibility of an erroneous measurement in the published value is supported by measurements by Schewe\textsuperscript{21} where the uni-axial stress state value was found to be $-35 \times 10^{12} \text{(C/m}^2\text{)/Pa}$.
Several other interesting points can be observed from the calibration studies. First, there is a fall-off in response for frequencies below 5 Hz. At frequencies above 5 Hz, no frequency dependence is observed over the tested frequency range. Second, the precision of the results for Plexiglas-containing specimens is very good, with differences in calibration slope no greater than 1.5 percent at any tested frequency among any given batch of KYNAR® film. Differences in the film sensitivity due to batch variation in the manufacture of the film have been observed by the authors and can be as large as 10 percent. Thus, it is important to calibrate each lot of film used. The linear regression slopes are useful as calibration constants relating the measured voltage outputs to the average stresses at the stress sensor locations.

F. EMPLOYMENT IN VARIOUS ADHESIVE JOINTS

The film sensors were used to determine peel stress variations in single lap joints. Single lap joints with graphite/epoxy adherends and an epoxy adhesive were made with a multi-point stress sensor film embedded within the 25.4 mm bond length. The film contained seven active sensors with dimensions of 0.79 mm by 12.7 mm spaced along the length of the bond. Care was taken to align the less sensitive 2-direction of the film with the loading axis in order to lessen the in-plane normal stress contributions to the output voltage. The joints were then cyclically loaded in a
sinusoidal manner at a stress amplitude of 0.345 MPa based on the bond area. The loading took place about a mean tensile stress of 0.345 MPa in order to assure tensile-tensile loading and thus prevent possible buckling of the specimens which may result from compressive loading.

Due to the high modulus of the laminate in the line of the load ($E_1 = 200$ GPa) and the film orientation in the bond, very little contribution to the voltage by in-plane stresses was expected. Thus, the results obtained from the sensors were converted from the measured voltages to stresses using the metal calibration constants.

The resulting sensor stresses were then compared to a finite element analysis of the single lap joint. The finite element analysis was performed using ABAQUS commercial software. The adhesive bondline was modeled with plane-strain linear elements, and a geometrically nonlinear analysis was performed. There were five elements through the adhesive thickness and sixty along the bond length. The elements were center-biased at a ratio of four-to-one along the length in order to reduce the element size near the bond termini where the stress concentrations are located. The largest aspect ratio of any element in the model was 13.4, occurring in fairly constant regions of low stress. In the regions of stress concentrations, the aspect ratios of the elements were less than four. Mesh refinement and biasing were also performed on the adherend models in order to match the elements in the adhesive
layer and alleviate the need to introduce transition elements. Since the joint was
loaded sinusoidally, separate analyses were performed at loading conditions
representing the peak and valley loads. The sensors would be expected to measure the
difference between the two stress distributions.

The in-plane stress distribution along the load axis was also calculated in the
sensor region from the finite element analysis. Assuming the in-plane transverse
stresses were related to the load-axis stresses by the Poisson’s ratio of the adherend,
the in-plane stress contributions to the voltages were calculated using published values
of the uniaxial strain piezoelectric constants\textsuperscript{21}. The in-plane stress voltage
contributions were found to be less than five percent of the total voltage throughout
the entire bondline. Thus, the in-plane contributions were neglected.

A comparison between the finite element analysis and the measurements
of the bond-normal stresses is shown graphically in Figure 5. In the figure the sensor
measurements are represented by the discrete points, and the finite element solution is
represented by the curve. The correlation between the measured and calculated
stresses is very good. The close correlation between the calculated and measured
stresses illustrates the utility of the measurement technique.
Figure 5. Comparison of measurements with finite element solution for bond-normal stress in a single lap joint.
The normal stress distribution in an elastomeric butt joint was also obtained using KYNAR® film stress sensors. A circular elastomeric disk of radius 27.7 mm and thickness 3.2 mm was bonded between two Plexiglas adherends. Keeping in mind the axisymmetry of the specimen, a piezoelectric film containing a simple grid of six stress sensors along a radial line was bonded into one of the Plexiglas-elastomer bonds. The sensor dimensions were 3.2 mm by 3.2 mm. The joint was loaded in compression using a sinusoidal wave input of 20 Hz and varying dynamic stress amplitudes between 0.28 and 0.74 MPa. This particular joint was chosen because there exists a closed-form analytical solution to the radial distribution of normal stress discussed by Gent and Meinecke\textsuperscript{22}. The closed-form solution closely approximates finite difference solutions for the given specimen except at the outer radial position where finite element solutions predict singular normal stresses\textsuperscript{23}. The normal stresses measured by the six stress sensors are compared with the analytical solution in Fig. 6. The comparison of the experimental results with the analytical model shows correspondence to within 10 percent over the entire range of radial position for which the closed-form solution and finite element solutions coincide. In the form used, the closed-form solution contains only easily measured geometric parameters with no adjustable parameters. Thus, Fig. 6 does not represent a curve fit; rather, it is a graphic illustration of the potential of the proposed technique.
Figure 6. Sensor measurements compared with the analytical solution for the normal stresses in an elastomeric butt joint.
G. CONCLUSIONS

Peel stresses are critical stresses in a variety of adhesive joints. Metallized poly(vinylidene fluoride) films were etched to provide multi-point peel stress sensors which can be embedded within adhesive joints to measure these important stresses. Photolithographic pattern transfer was been used and offers the potential to miniaturize the stress sensors. Although the approach requires dynamic loading and has temperature and load restrictions, calibration studies have revealed that the output is quite linear and very reproducible. Comparison of measured stresses in elastomeric butt joints and single lap joints with accurate closed-form and finite element solutions show convincingly the applicability of the proposed technique.

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I. REFERENCES


SECTION 5. SUMMARY

The ability of researchers to predict bond strengths of many adhesive joints, including several joints loaded in shear, using mode I fracture parameters has clearly illustrated the importance of peel or normal stresses in adhesive joints. At the same time, there exist very limited means of measuring the bond-normal stresses. The few methods available are very complicated laboratory methods whose applicability is limited due to their sophistication. In an effort to improve the ability to measure normal stresses, piezoelectric poly(vinylidene fluoride) (PVF$_2$) film was investigated as an in situ sensor for measuring bond-normal stresses.

KYNAR® piezoelectric PVF$_2$ film manufactured by Atochem (formerly Pennwalt) was employed in the study. The film used was 52 µm thick and was commercially coated with a thin vapor-deposited layer of constantan (a copper-nickel alloy) on both surfaces. The metal coating aids in the poling of the film during its manufacture and is also needed as an electrically-conductive path for stress sensor measurements. When subjected to a change in the normal strain in any of the three principal material directions, the piezoelectric film produces an open circuit voltage proportional to the magnitude of the change in strain. The principal material directions of the film are the plane-normal direction and two mutually perpendicular directions in the plane of the film. The induced voltage diminishes with time, making the measurement of residual and static stresses beyond the capability of the film.
The open circuit voltage is measurable only over areas where the deposited metal layer remains on both surfaces of the film. Thus, multiple discrete sensors can be made from a single section of film by protecting the metallization areas desired for sensors and sensor leads and etching the remaining metal away. The sensor film, containing a multiple sensor grid, could then be introduced into the bondline prior to cure, and the normal stresses developed in the bondline as the joint was loaded after cure could then be measured from the voltages that were induced piezoelectrically.

The actual construction of the multi-point sensors was performed in two ways. The desired metallization areas were protected by either thin adhesive border tape or exposed photoresist. The adhesive border tape application resulted in fairly crude, but very easily fabricated sensors. Using the photoresist as part of the photolithographic pattern transfer technique provided refined, miniaturized stress sensors. Sensors as small as 0.25 mm wide were made using the technique. In both cases the unprotected metallization was removed in a ferric chloride etch using standard circuit board etchant.

One problem encountered in the study was that of embedding the film in the bondline without significantly reducing the strength of the joint. It was found early in the project that embedding the sensors within the bondline reduced single lap joint
strengths by more than 50%. Much effort was made to improve the bond strength to the PVF₂ employing various plasma pretreatments and an acid etch.

Oxygen, nitrogen, argon and ammonia plasmas and an 80% Brite Dip solution (70% acetic acid, 26% phosphoric acid, and 4% nitric acid) were used to modify the PVF₂ surface. Contact angle measurements and XPS surface analyses were performed on the pretreated surfaces in order to measure changes in the surface energetics and surface chemistry. In order to assess improvements in bonding to the pretreated surfaces, 180° peel and tapered double cantilever beam (TDCB) specimens were employed.

Oxygen plasma was found to be too aggressive for piezoelectric stress sensor applications, but could possibly be used on the unmetallized film. Argon and argon followed by ammonia plasma pretreatments produced the best peel strengths of the plasma treated films with peel strengths between 24 and 27 N/m. The acid etched film provided a peel strength of 48 N/m. These peel strengths represented a substantial increase 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 fracture toughnesses compared well with TDCB specimens bonded with the same adhesive without embedded film which yielded an average value of 437 N/m.

Importantly, 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 \textit{in situ} stress sensor applications.

In order to understand the relationship between the induced voltages measured and the normal stresses at the sensor locations, a series of tests were performed to calibrate the film using a charge amplifier and a storage oscilloscope. A tensile butt joint specimen was found to be well suited for the calibration since the local normal stresses do not vary more than one-and-a-half percent from the average normal stress within the inner portion of the bond. The joint containing a small sensor located at the center of the bondline was subjected to varying magnitudes of sinusoidal normal stresses. Steel adherends were used both with and without Plexiglas spacers in order to observe the effect of in-plane strains which add to the induced voltages. The piezoelectric sensitivities were determined to be 252 and 168 mV/MPa for the Plexiglas and steel respectively. With the use of an electrometer, the capacitance of the charge amplifier was determined allowing the calculation of the piezoelectric strain constants from the measured sensitivities. The plane-normal strain constants were -33
and -22 pC/m²/Pa which coincide with the published values of the constants for the cases of fully constrained and unconstrained in-plane film deformation, respectively.

The sensitivities were measured over a large range of mean normal stresses and varying frequencies. There appeared to be no mean stress effect and no dependence on frequency between 5 and 30 Hz. Below 5 Hz, however, the measured voltages (and, hence, piezoelectric sensitivities) decreased. At 0.25 Hz the voltages could not be accurately measured with the charge amplifier and oscilloscope.

In addition, strips of the film cut in the two in-plane principal directions of the film were cyclically loaded in order to determine the in-plane sensitivity of the film. The measured sensitivities correlated to piezoelectric stress constants of 23.3 and 2.9 pC/m²/MPa which again relate well to the published values of 23 and 3. In all sensitivity measurements, the induced voltages were found to dependent on the applied dynamic load in a highly linear manner.

The film is theoretically insensitive to shear stress. In order to assure this experimentally, sensors were bonded into napkin ring specimens which were then loaded in torsion. The measured sensitivities were about 4% of the measured plane-normal sensitivities (measured with Plexiglas spacers) and were assumed to be due to normal loads induced in the specimen during testing.
The sensors were employed in single lap shear and tensile butt joints. Single lap joints with graphite/epoxy adherends and an epoxy adhesive were made with the multi-point stress sensor film embedded along the 25.4 mm bond length. The film contained seven active sensors with dimensions of 0.79 mm by 12.7 mm spaced along the length of the bond. The joints were then cyclically loaded in a sinusoidal manner at a stress amplitude of 0.345 MPa based on the bond area. The loading took place about a mean tensile stress of 0.345 MPa in order to assure tensile-tensile loading and thus prevent possible buckling.

The results obtained from the sensors were converted from the measured voltages using the calibration results without the Plexiglas spacers due to the constraint imposed on the film by the composite material adherends. The resulting sensor stresses were then compared to a finite element analysis of the single lap bond-normal. The measurements correlated very well with the analysis.

The normal stress distribution in an elastomeric butt joint was also obtained using the KYNAR® stress sensors. A circular elastomeric disk of radius 27.4 mm and thickness 3.2 mm was bonded between two Plexiglas adherends. Keeping in mind the axisymmetry of the specimen, a piezoelectric film containing a simple grid of six stress sensors along a radial line was bonded into one of the Plexiglas-elastomer bonds. The joint was loaded in compression using a sinusoidal wave input and
varying dynamic stress amplitudes between 0.28 and 0.74 MPa. The normal stresses measured by the six sensors were compared with a closed-form analytical solution. The comparison shows correspondence between the measured values and the calculated values to within 5% over the entire range of radial position for which the closed form solution is valid. It should be noted that the closed-form solution used contains no adjustable parameters. Thus the close correspondence results from the accuracy of the stress sensor measurements rather than a curve fit.

Finally, work was performed to investigate the use of the metallized surface layers as resistance strain gages. By etching resistance strain gages in the in-plane principal material directions, a strain sensor that would measure the strains in three orthogonal directions could result. The in-plane strains would be measured by the resistance changes of the gages etched in the top and bottom metallization surfaces of the film, and the plane normal strain would be measured piezoelectrically. In order to investigate the feasibility of the resistance gages, five 1/8 inch wide 2 inch long metal strips were etched from the surface of the piezo film. The gages were then bonded to the surface of a aluminum plate which was then strained. The average value of the ratio of the normalized change in resistance to the strain in the sensor (the gage factor) was found to be 2.5. Thus, the use of the film as a three-dimensional strain gage appears to be quite promising.
The uses of the sensors appear to be many and varied. On a laboratory scale, the sensors could be miniaturized using the photolithographic pattern transfer technique in order to measure the order of stress singularities. The photolithographic pattern transfer technique would need to be refined and optimized. Sensors made to date using this technique did not have well-defined edges suggesting the need for sharper contrast of the photolithographic patterns or a chemical photoresist more impervious to the etchant.

The sensor may also find use in back-calculating the Poisson's ratio of elastomers. By using the sensor to measure tensile stresses at the center of elastomeric butt joints, the Poisson's ratio of the elastomer material could be calculated since the center-line stress is highly dependent on the Poisson's ratio at values between 0.498 and 0.50. At levels below 0.498, the difference in stress lessens considerably with changes in the Poisson's ratio, making accurate determination of the ratio much more dependent on the precision of the stress measurement. In preliminary studies, the elastomeric materials selected were found to have Poisson's ratios in the 0.47 to 0.495 range. An accurate determination of the ratios was not possible due to the relatively low values of the Poisson's ratio and the ten-to-fifteen percent variability in the stress measurements. The technique does have merit, however, for materials with Poisson's ratio closer to 0.50.
The industrial applications of the film are significant. The film can be used in any adhesive bonds which are cured at room or slightly elevated temperature, and which are subjected to significant transient loads. A good example of this is rocket motor components. In order to reduce thermal residual stresses, room-temperature-cure structural adhesives are commonly used. In addition, the bondlines are loaded at extremely high rates during motor ignition. The PVF$_2$ piezoelectric sensors are being considered for use in flight simulation motors at Thiokol Corporation in order to verify the structural analysis of nozzle bondlines. This is just one example of a practical industrial application of the sensor. The sensor utility is limited only by the previously stated restrictions.
APPENDIX A. Piezoelectric Film Shear Insensitivity

The piezoelectric stress and strain constants are third order tensors which relate the second order tensors (tensors) of applied or induced stress or strain to the first order tensors (vectors) of induced electrical field, for the stress tensor, and applied electrical field, for the strain field. As third order tensors, both piezoelectric constants have twenty-seven components.

Due to the symmetry of the stress and strain tensors and the material symmetry of the piezoelectric film, the number of independent, non-zero components is greatly reduced. The following discussion will show the reduction of independent non-zero components for the piezoelectric stress constants, but the same arguments are valid in the reduction of piezoelectric strain constants.

The piezoelectric stress constants, $g_{ijk}$ relate the applied stresses, $\sigma_{jk}$, to the induced electrical field, $P_i$, by the following relationship:

$$P_i = g_{ijk} \sigma_{jk}. \quad (A-1)$$

Since the piezoelectric stress constants form a third order tensor, $g_{ijk}$, they transform upon changes of axes to $g'_{lmn}$, where:
and $a_{ii}$, $a_{mj}$, and $a_{nk}$ are transformation tensors of unit magnitude. In the piezoelectric film used as sensors in this study there exist two planes of symmetry: the 2-3 plane and the 1-3 plane (direction numbers are in the principal material directions). Due to the planes of symmetry, two unique transformations reveal that many of the twenty-seven piezoelectric stress constants making up the third order tensor are identically equal to zero. Tensor transformations through a plane of symmetry result in identically equivalent tensors ($g'_{lnm} = g_{ijk}$).

In the case of the 2-3 plane of symmetry, the three transformation tensors in the transformation equation become:

$$
a_{ij} = \begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
$$

By performing the transformation according to Equation A-2, the following equalities will result:

$$
\begin{align*}
g_{111} &= -g_{111} & g_{122} &= -g_{122} & g_{123} &= -g_{123} \\
g_{132} &= -g_{132} & g_{333} &= -g_{333} & g_{212} &= -g_{212} \\
g_{213} &= -g_{213} & g_{221} &= -g_{221} & g_{231} &= -g_{231}
\end{align*}
$$
The only way in which the above equalities can hold true is for the thirteen components above to be identically equal to zero. This reduces the number of non-zero piezoelectric stress constants from twenty-seven to fourteen.

By performing the same transformation through the 1-3 plane of symmetry, with the transformation tensors

\[
a_{ij} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{(A-4)}
\]

the following components can be shown to be identically equal to zero:

\[
\begin{align*}
\varepsilon_{112} &= -\varepsilon_{112} \\
\varepsilon_{121} &= -\varepsilon_{121} \\
\varepsilon_{211} &= -\varepsilon_{211} \\
\varepsilon_{222} &= -\varepsilon_{222} \\
\varepsilon_{233} &= -\varepsilon_{233} \\
\varepsilon_{323} &= -\varepsilon_{323}.
\end{align*}
\]

This reduces the number of non-zero components of the piezoelectric stress tensor from fourteen to seven.
The seven non-zero components of the piezoelectric stress tensor are: \( \varepsilon_{113}, \varepsilon_{131}, \varepsilon_{223}, \varepsilon_{232}, \varepsilon_{311}, \varepsilon_{322} \) and \( \varepsilon_{333} \). In addition to the planes of material symmetry, the stress tensor is also symmetric. Due to this symmetry, the following equalities hold for the piezoelectric stress tensor:

\[
\varepsilon_{113} = \varepsilon_{131} \quad \text{and} \quad \varepsilon_{223} = \varepsilon_{232}.
\]

This leaves only five independent non-zero components of the piezoelectric stress tensor.

Also due to the symmetry of the stress tensor, the piezoelectric stress tensor can be written in contracted indicial notation \( \varepsilon_{\alpha \beta} \), where the subscript \( \alpha \) ranges from one to three and the subscript \( \beta \) ranges from one to six, with the following subscript identities, in the form normal notation contracted notation: 11 ... 1, 22 ... 2, 33 ... 3, 23 ... 4, 13 ... 5 and 12 ... 6. In contracted indicial notation, the independent non-zero components of the piezoelectric stress tensor are:

\[
\varepsilon_{\alpha \beta} = \begin{bmatrix}
0 & 0 & 0 & 0 & \varepsilon_{15} & 0 \\
0 & 0 & 0 & \varepsilon_{24} & 0 & 0 \\
\varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} & 0 & 0 & 0
\end{bmatrix}
\]  
(A-5)
Because the piezoelectric material is manufactured as a thin film with metal vapor deposited on the two surfaces in the 1-2 plane, the induced electric field is only measurable in the 3-direction. Thus, the three components of the piezoelectric stress tensor which are of interest when employing KYNAR® piezoelectric film are $g_{31}$, $g_{32}$ and $g_{33}$, which represent the electric field induced through the thickness of the film when normal stresses are applied to the film in its three principal material direction. No electrical field perpendicular to the plane of the film will be produced by applied shear stresses due to the symmetry of the film.

In order to verify that the film is manufactured with the previously discussed planes of symmetry, a section of the film with four etched sensors was bonded into the bondline of a "napkin" torsion ring adhesive specimen. The sensors were etched in the film in such a way that two sensors would measure the sensitivity of the film to $\tau_{13}$ and two would measure the $\tau_{23}$ film sensitivity. The napkin ring specimen is shown in Figure A-1. This specimen was chosen due to the very small amount of bond-normal stress induced in the specimen during testing.

The results of the testing are shown in Figure A-2. The sensitivities of the film where determined by linear regression of the data. The sensitivities were found to be 7.1 mV/MPa and 3.1 mV/MPa for $\tau_{23}$ and $\tau_{13}$ stresses respectively. These sensitivities, however, are more likely due to induced bond-normal stresses caused by the necessity
Figure A-1. Schematic drawing of napkin ring specimen geometry.
of holding the napkin ring adherends in a fixed axial position with respect to one other during the testing. This would be expected to induce bond-normal stresses in the adhesive layer during torsion testing.

The axial strain due to the second order effect of the rotational shear strain was calculated using the following equation:

\[
\varepsilon_{zz} = \frac{\partial u_z}{\partial a_z} + \frac{1}{2} \left[ \left( \frac{\partial u_r}{\partial a_z} \right)^2 + \left( \frac{\partial u_\theta}{\partial a_z} \right)^2 + \left( \frac{\partial u_z}{\partial a_z} \right)^2 \right]
\]

where \( \varepsilon_{zz} \) is the axial strain, \( u_i \) are the displacements and \( a_i \) are the unit directional vectors. The term \( u_z \) is equal to zero, because the testing device held the adherends fixed axially. The second and third terms represent the square of the shear strain, \( \gamma \), in the \( r \) and \( \theta \) directions on the \( z \) face. The \( \gamma_{zz} \) term is negligible, but \( \gamma_{oz} \) is the shear strain related to the rotational shear. At a shear stress of 2.0 MPa, the resulting axial strain is 3.6 microstrain. Using the measured through-the-thickness film sensitivity, the calculated induced voltage is only 2.4 mV, which represents 20 to 40 percent of the measured voltage. The remainder of the measured signal may be due to electrical noise.
APPENDIX B. Measurements of In-plane Piezoelectric Sensitivities

In order to measure the in-plane sensitivity of the KYNAR® film, six four-inch by five-eighths inch specimens were cut from sheets of the piezoelectric film. The specimens were in two groups of three cut in the one- and two-direction of the film. In order to measure the variability of the film, one specimen was cut in each principal material direction from three separate sheets of the film. It is unknown for certain whether the individual sheets came from separate manufactured batches of the film, but it is probable that the three sheets came from the same batch. Three sensors one-eighth inch wide were etched in each specimen across the width of the specimen.

The ends of the specimens were bonded into aluminum end pieces as shown in Figure B-1 to obtain a clamped boundary condition without the possibility of grip slippage. The end pieces were then secured in the MTS, and the specimens were cyclically loaded in tension at 10 Hz.

The leads were attached to the sensors using toothless miniature alligator clamps. The clamps were first overlapped in order to keep the film from bending through its width due to the weight of the clamps. The induced voltages were filtered through the charge amplifier and recorded from the storage oscilloscope.
Figure B-1. Specimen geometry used for in-plane piezoelectric sensitivity measurements.
The results of these tests are shown in Figures B-2 and B-3 for the one- and two-directional film sensitivities, respectively. The sensitivity measurements appear to be very reproducible. The values of the three one-direction in-plane piezoelectric sensitivity measurements averaged 0.0171 V/m/Pa with a 5.3% coefficient of variation. Those of the two-direction averaged 0.00216 V/m/Pa with a 7.4% coefficient of variation.

After using the electrometer to measure the effective capacitance of the charge amplifier and electrical leads, the in-plane piezoelectric strain constants were calculated from the measured sensitivities and compared with the values published in the KYNAR® Piezo Film Technical Manual. The calculated constants were 23.3x10^{12} and 2.9x10^{12} (C/m^2)/Pa for the one- and two-directions respectively. These values compare well with the published values of 23x10^{12} and 3x10^{12} (C/m^2)/Pa. The values were calculated by multiplying the measured sensitivities by the film thickness, the effective capacitance of the charge amplifier and leads (1.321x10^9 f), and the reciprocal of the sensor area (0.078 in^2).
Figure B-2. Measured piezoelectric sensitivity in the transverse in-plane direction of the film.
Figure B-3. Measured piezoelectric sensitivity in the stretched in-plane direction of the film.
APPENDIX C. Measurement of Signal Contribution from Electrically Coupled Sensors

In order to verify the need to electrically isolate each sensor, a simple sensor grid was etched. The grid consisted of a strip of metal left on one side of a four-inch by four-inch piece of film and six metal strips left on the opposite side of the film etched perpendicular to the first strip as shown in Figure C-1. The sensor was sandwiched between two three-and-one-half-inch diameter elastomer disks one-eighth-inch thick. An ex was marked on one of the disks towards the edge in order to create a reference point for aligning the sensor between the disks. Sensor number one, shown in Figure C-1, was placed over the ex with sensors two through six extending towards the center of the elastomer sandwich in such a way that all the sensors extended beyond the sandwich.

The sandwich was then placed in the MTS, centered between two three-and-three-quarter-inch diameter steel platens. The sandwich was cyclically (sinusoidal wave) loaded in compression at 10 Hz, and the induced voltage was measured from sensor one using the charge amplifier (gain set at one) and the storage oscilloscope.

After making the measurement, the sandwich was unloaded, removed from the MTS and disassembled. Sensor number six was then removed by etching the sensor grid up to sensor number five. The sandwich was then reassembled and loaded as
Figure C-1. Sensor grid employed in signal contribution test.
before. The induced voltage at sensor one was again measured and recorded. The sole physical difference from the arrangement during the previous test was that of the removal of sensor six which, along with sensors two through five, was suspected of adding to the signal measured at sensor one.

Following this procedure, sensors two through five were systematically removed between tests. The measured output voltages are shown graphically in Figure C-2 where the number of contributing sensors denotes the number of sensors linked by the common lead. The increase in measured voltage with an increasing number of sensors was too large to be attributable to inexactness in the alignment of the sensor grid within the sandwich. Thus, it was concluded that sensors within a grid must be electrically isolated from each other in order to obtain unconfounded measurements.
Figure C-2. Measured output voltage at same sensor, compared with number of sensors linked by common electrical lead.
APPENDIX D. Data Reduction of Bond-Normal Stress Measurements in Adhesive Joints

Voltage measurements made using the piezoelectric sensors were easily converted to local stresses employing the following simple equation:

\[
\text{Stress} \approx \frac{\text{Voltage} \cdot \text{Calibration Sensor Area}}{\text{Sensor Sensitivity} \cdot \text{Sensor Area}}
\]  

(D-1)

The sensor sensitivity employed depended on the adhesive specimen in which the bond-normal stresses were measured. That used to reduce the single lap joint data was the average sensitivity measured by the calibration specimen without Plexiglas spacers. This constant was used because the stiff composite adherends were expected to constrain in-plane deformation of the film sensors. The sensitivity employed in the data reduction of the elastomeric butt joint specimens was that obtained employing the Plexiglas spacers in the calibration specimen, which was different from the elastomeric butt joint only in the elastomeric disk bonded between the Plexiglas spacers. The incorporation of the sensor areas in the calculations is due to the use of the charge amplifier (which was not used in the preliminary studies discussed in the first paper).
APPENDIX E. Finite Element Analysis of the Influence of an Embedded Sensor on Bond- Normal Stresses in a Single Lap Joint

It is important to understand the influence of the embedded sensor on the surrounding stress field. In order to obtain good correlation between predicted and measured stress, the sensor should not perturb the surrounding stress field significantly. This is especially important in using the sensors as a tool for verifying finite element analyses of large intricate structural joints. In this case the analyses are performed on meshes which are not refined to the extent necessary to incorporate the sensor into the model. To do so would be costly. The influence of the sensor on the surrounding stress field is also important when using a sensor which does not span the entire bondline.

In order to determine the effect of the sensor on the stress field, a parametric study was performed using finite element analysis of the single lap joint model used for comparison with measurements in Section 3. As the mechanical properties of the adhesive, namely Young's modulus and Poisson's ratio, diverged increasingly from those of the sensor (modulus: 2.3 GPa and Poisson's ratio: 0.25), it was expected that the surrounding stress field would be increasingly perturbed. Thus, a three-by-three matrix was set up with adhesive modulus and Poisson's ratio as the parameters. The values input for the modulus were 0.035, 0.35 and 3.5 GPa. The Poisson's ratios
were 0.20, 0.35 and 0.49. The matrix was run twice. The sole difference between the runs was in modeling the embedded sensor by using the PVF$_2$ material properties in the middle row of adhesive elements along the entire bondline. The element representing the adhesive were 46 µm thick which well represents the sensor film.

The bond-normal stress distributions, averaged from the nodes on the top and bottom surfaces of the middle row of elements, are shown in Figures E-1 through E-5. Figures E-1 and E-2 show the stresses from analyses with adhesive modulus equal to 3.5 and 0.35 GPa, respectively. It is significant that very little difference is observed in these figures due to the embedment of the film. This is especially important since the vast majority of epoxy adhesives have modulus values between these extremes.

Figures E-3, E-4 and E-5 illustrate the bond-normal stress distributions from analyses with a 35 MPa modulus and Poisson’s ratios of 0.20, 0.35 and 0.49, respectively. Although the sensor does not drastically alter the stresses, the perturbation is significant at the highest level of Poisson’s ratio. This is important since the Poisson’s ratio of lower modulus structural adhesives, eg. urethanes, approaches the 0.49 value.

In conclusion, the perturbation in the surrounding stress field caused by the embedment of the stress sensor into the adhesive bondline appears to be small,
Figure E-1. Influence of sensor on bond-normal stresses in a single lap joint (adhesive modulus 3.5 GPa).
Figure E-2. Influence of sensor on bond-normal stresses in a single lap joint (adhesive modulus 350 MPa).
Figure E-3. Influence of sensor on bond-normal stresses in a single lap joint.
Figure E-4. Influence of sensor on bond-normal stresses in a single lap joint.
Figure E-5. Influence of sensor on bond-normal stresses in a single lap joint.
especially for epoxy adhesives. The perturbation will increase, however, when using lower modulus, nearly incompressible adhesives.
APPENDIX F. The Theory of Piezoelectric Coefficients

There are, in general, four sets of piezoelectric coefficients which relate electromechanical coupling of applied or induced stress ($X_{ij}$) or strain ($x_{ij}$) and electric field ($E_i$, the voltage divided by the film thickness) or electric displacement ($D_i$, the charge per unit sensor area$^{1,2}$). These four sets of coefficients are defined as:

\[ d_{ijk} = \left( \frac{\partial D_i}{\partial x_{jk}} \right)_{E,T} = \left( \frac{\partial x_{jk}}{\partial E_i} \right)_{x,T} \]

\[ g_{ijk} = -\left( \frac{\partial E_i}{\partial x_{jk}} \right)_{D,T} = \left( \frac{\partial x_{jk}}{\partial D_i} \right)_{x,T} \]

\[ e_{ijk} = \left( \frac{\partial D_i}{\partial x_{jk}} \right)_{E,T} = -\left( \frac{\partial x_{jk}}{\partial E_i} \right)_{x,T} \]

\[ h_{ijk} = -\left( \frac{\partial E_i}{\partial x_{jk}} \right)_{D,T} = \left( \frac{\partial x_{jk}}{\partial D_i} \right)_{x,T} \]

where T refers to temperature which must remain constant in order to eliminate thermal stresses and strains. The constant temperature is also important when dealing with PVF$_2$ which is pyroelectric as well as piezoelectric.

The first set of equalities in the above equations relates induced electric field or electric displacement to applied stress or strain, and are useful in sensor applications.
The second set of equalities relates induced stresses and strains to applied electric field and electric displacement, and are useful in actuator applications.

The sets of coefficients are interrelated as shown below:

\[
\frac{d_{ijk}}{g_{ijk}} = \frac{\varepsilon_{ijk}}{h_{ijk}} = \varepsilon_{ii} \\
\frac{d_{ijk}}{e_{ilm}} = \frac{g_{ijk}}{h_{ilm}} = S_{lmjk}
\]

where \( \varepsilon_{ii} \) is the permittivity of the material and \( S_{lmjk} \) is the material compliance. Thus, given any set of coefficients and the material permittivity and compliance tensors, all coefficient sets may be calculated.

Confusion can arise when the coefficient sets are improperly named. For example, the use of the term "piezoelectric stress constants" for the \( g_{ijk} \) set and "piezoelectric strain constants" for the \( d_{ijk} \) set in the KYNAR® Piezo Film Technical Manual leads to the mistaken belief that the two sets are related by the material compliance instead of the permittivity.
An understanding of the definitions of the coefficients and their interrelationships is very important in developing and using the piezoelectric stress sensors. In calibrating the film, a known stress amplitude was applied to the film and the voltage through the film thickness was measured. Since a charge amplifier was used to make the measurements, the measured voltages were actually a measure of the charge generated at the sensor location divided by the capacitance of the charge amplifier and electrical leads. Thus, although a voltage was measured, the coefficient set being tested was actually the $d_{ijk}$ set.

In considering the signal contribution of the in-plane stresses and strains, it is important to use the $e_{ijk}$ coefficient set. Since $d_{ijk}$ and $g_{ijk}$ coefficients are determined in states of uniaxial stress, a portion of the induced electric field or electric displacement is caused by strains in all three principal material directions due to the Poisson effect. By using the $e_{ijk}$ coefficients, the influence of stresses and strains in the principal material directions can be calculated independently. This allows the in-plane-stress voltage contributions to be quantified and factored out once the in-plane stress or strain distribution has been determined.


VITA

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