AMMRC TR 77-2

PIEZOELECTRIC POLYMER FILMS FOR APPLICATION IN **MONITORING DEVICES**

AD

RICHARD J. SHUFORD, ANTHONY F. WILDE, JOHN J. RICCA, and GEORGE R. THOMAS ORGANIC MATERIALS LABORATORY

February 1977

。 這些你說我這些意思了。」「這些是的最高級要認識的。 這些的意思。」

COPY

Approved for public release; distribution unlimited.

ARMY MATERIALS AND MECHANICS RESEARCH CENTER Watertown, Massachusetts 02172

 3

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Mention of any trade names or manufacturers in this report shall not be construed as advertising nor as an official indorsement or approval of such products or companies by the United States Government.

DISPOSITION INSTRUCTIONS

Destroy this report when it is no longer needed. Do not return it to the originator.

2. GOVT ACCESSION NO	. 3. RECIPIENT'S CATALOG NUMBER
and a second sec	TYPE OF REPORT & PERIOD COVE
FOR APPLICATION	(Dring) Pont
· Frank and Annual And	6. PERFORMING ORG. REPORT NUMBE
· • · •	8. CONTRACT OR GRANT NUMBER(s)
F./Wilde,	V200
Thomas	(6)
RESS	10. PROGRAM ELEMENT, PROJECT, TA
Research Center	D/A Project: /1T163102D07
14	AMCMS Code: 613102.12.15
	AVENCY ACCESSION: DA OF47
ent and Readiness	())Febrand 1977
a 22333	13. NUMBER OF PAGES
Iterent from Controlling Office)	15. SECURITY CLASS. (OF THIS report)
	Unclassified
	SCHEDULE
nerea in block 20, 11 dilleteni ifa	m ny porij
<u></u>	
cience Conference,	U.S. Military Academy,
976. Published in	the Proceedings of the
, v. 3, June 1976,	p. 217.
ery end identily by block number)	
ctric field	Vibration sensor
ferred orientation	Strain gage
rophone	Medical sensor
ry and identify by block number)	
SEE DEVEDSE SIDE)	
	403105
	F./Wilde, /Thomas /RESS Research Center 72 ent and Readiness a 22333 //erent from Controlling Office) listribution unlimit /ered in Block 20, if different fro // Element from Conference, 076. Published in , V. 3, June 1976, // end identify by block number) // erric field ferred orientation rophone // end identify by block number) SEE REVERSE SIDE)

a second seco



Block No. 20

ABSTRACT

This

To develop Army applications based on the pronounced piezoelectric effect noted for polyvinylidene fluoride (PVF2), our laboratory has conducted a systematic investigation of factors responsible for this remarkable behavior of an organic polymer. Commercial PVF_2 homopolymer and copolymer films were oriented by uniaxial stretching, biaxial stretching, or rolling. The oriented films were characterized by means of infrared spectroscopy, density, birefringence, sonic modulus, and X-ray diffraction. The oriented films were then poled at various electric field strengths and temperatures for various times. Trends have been noted between draw ratio and the resulting physical properties; the piezoelectric activity has been correlated with draw ratio and poling conditions. The piezoelectric activity has also been investigated after accelerated temperature aging and isothermal aging. Prototype devices have been fabricated at AMMRC with these films to demonstrate their potential utility in microphones, vibration sensors, and strain gages. Further development efforts have been conducted jointly with industrial firms to produce more refined prototype devices, including a remarkable medical sensor. It is concluded that piezoelectric polymer films can provide unique and advantageous solutions to a number of Army problems requiring monitoring and communication devices.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

South Completion States and

PREFACE

We are grateful to the Society of Plastics Engineers for permission to use Figures 1 to 6 and Table 1 which originally appeared in Polymer Engineering and Science, volume 16, 1976, page 25.

2

Achievalin fut WARA SE 0 ball Section 0 NTIS 00**C** BRAY HAR ED INSTIFICTION OISTRIBUTION/AVAILABILIET 400 Will IN/ THEM 11 0181

In Subscript State

and the second second

CONTENTS

and the second second second second

'n

おうご とういう

A State of the state

فالأفار الأراد والمروا والمناطق ومداد فالطوم والمروي

	Page
PREFACE	iii
INTRODUCTION	1
EXPERIMENTAL	1
RESULTS AND DISCUSSION	2
APPLICATIONS	9
Microphones	9
Vibration Sensors	10
Strain Gages	. 11
Medical Sensors	11
Other Proposed Applications	12
FUTURE INVESTIGATIONS	12

INTRODUCTION

A piezoelectric material produces an electrical signal when subjected to a mechanical stress. Traditional examples of this effect have been demonstrated by certain ceramic materials and inorganic crystals. Recently certain organic polymers, when properly treated (by both orientation and polarization) have exhibited this phenomenon. 1-4 The purpose of our research in piezoelectric polymers is to prepare and characterize organic polymer films for evaluation as transducer elements in devices, such as microphones, accelerometers, strain gages, and medical sensors. The large piezoelectric effect for polyvinylidene fluoride (PVF2) and its copolymers suggests that they are good candidates for such devices. Therefore our approach has been to impart and to comprehensively study systematic changes in the structure and morphology of PVF_2 and to relate these to subsequent piezoelectric behavior in an attempt to understand, optimize, and utilize the piezoelectric phenomenon.⁵ Commercially available PVF₂ homopolymer and copolymer films were oriented by various techniques including uniaxial stretching, biaxial stretching, and rolling. The resulting films were characterized by infrared spectroscopy, density, birefringence, sonic modulus, and X-ray diffraction. The oriented films were then poled at various electric field strengths, temperatures, and times. Correlations were made between draw ratio, physical properties, poling conditions, and piezoelectric activity of the films. The piezoelectric activity was also investigated as a function of subsequent temperature conditioning and temperature cycling. Prototype devices employing these polymer films as transducing elements have been fabricated and tested.

EXPERIMENTAL

Extruded homopolymer PVF_2 film (Kynar, Pennwalt Corp.) was obtained from Westlake Plastics. This polymer film was oriented to varying degrees (machine draw ratios from 2/1 to 7/1) by uniaxial stretching at high speed in a radiant heated oven according to a procedure developed in this laboratory.⁶ Extruded copolymer polyvinylidene fluoride-tetrafluoroethylene (Kynar 7200) PVF₂-TFE was obtained from Pennwalt Corp. The copolymer film was oriented to various degrees up to about 4/1 by stretching in an Instron test machine at room temperature.

Infrared spectra of the homopolymer and copolymer films were recorded in the far infrared region. Densities of the polymer films were determined with a gradient density column. Total birefringence of the oriented polymer films was obtained by standard interferometric techniques. Sonic modulus of the films was determined by using a dynamic modulus tester. Wide angle X-ray diffraction photographs of the PVF_2 films were obtained with CuKa radiation on a flat plate camera.

- 1. KAWAI, H. The Piezoelectricity of Polyvinylidene Fluoride. Japan J. Appl. Phys., v. 8, 1969, p. 975.
- 2. FUKADA, E., and TAKASHITA, S. Piezoelectric Effect in Polarized Polyvinylidene Fluoride. Japan J. Appl. Phys., v. 8, 1969, p. 960.
- 3. HAYAKAWA, R., and WADA, Y. Piezoelectricity and Related Properties of Polymer Films. Adv. Polym. Sci., v. 11, 1973, p. 1.
- 4. BROADHURST, M. G. Proceedings of Plezoelectric and Pyroelectric Symposium Workshop. Coordinator, National Bureau of Standards, NBSIR 75-760, September 1975.
- SHUFORD, R. J., WILDE, A. F., RICCA, J. J., and THOMAS, G. R. Characterization and Piezoelectric Activity of Stretched and Poled Polyvinylidene Fluoride. Part 1: Effect of Draw Ratio and Poling Conditions. Polym. Eng. Sci., v. 16, 1976, p. 25.
- 6. DESPFR, C. R., LIONETTA, W. G., and LEWIS, R. W. Radiant Oven Stretching Process for Thin Film Polymeric Armor Material. Army Materials and Mechanics Research Center, AMMRC TN 74-11, September 1974.

alphania and an a

Polymer films were poled by placing them between two copper poling plates (embedded in two electrically insulating blocks), clamped together and placed in a controlled temperature oven preheated to 100 to 110 C. The poling plates were connected to a high-voltage power supply. After 30 minutes poling time at poling fields of 500 or 1000 kV/cm, the maximum film temperature was between 80 and 85 C. The sample was cooled with the field applied for at least 15 minutes, at which time the final film temperature was between 65 to 70 C.

The static piezoelectric constant was obtained by placing known compressive loads upon the stretched and poled polymer film and measuring the resultant stressinduced charge with an electrometer. From the incremental values of static compressive load on the polymer film and the corresponding generated charge, we calculated the piezoelectric constant (d_{33}) by the expression $d_{33} = charge/load$, in units of coulombs/newton.

The dynamic tensile piezoelectric activity was determined by a test system which we developed for measuring the complex piezoelectric stress and strain constants and complex elastic moduli of polymer films. One end of the metallized film was held stationary by a clamp attached to a force transducer; the other end of the film was fixed to an electromagnetic shaker table by means of a combination clamp and accelerometer mount. The resulting stress-induced electrical output from the polymer film was monitored with a charge amplifier and a frequency response analyzer. These instruments provided values of the magnitude of the generated charge and its phase relationship to the applied stress on the film, from which we calculated the complex tensile piezoelectric strain constant (d^*_{31}) in units of coulombs/hewton. In addition, double integration of the measured acceleration led to values of the strain in the film which permitted the calculation of the complex tensile piezoelectric stress constant (e^*_{31}) in units of coulombs per square centimeter.

RESULTS AND DISCUSSION

It was found that systematic increases in the degree of PVF_2 film orientation produced systematic changes in the properties of the film. These property changes were characterized by a number of methods and are listed in Table 1.

Draw Ratio	Thickness (mils)	Density (g/cc)	Birefringence (n _{ll} - n <u>l</u>)	Sonic Modulus (ksi)	Crystalline Conformation	PZ Constant [†] (pcoul/nt)
Orig.	5,40	1.768	0,0045	326	Phase II	2.2
2/1	3,55	1,770	.022	338	+	6,2
3/1	3.25	1.773	.026	362	†	5.1
4/1	2,90	1.778	,031	370	†	8,5
5/1	2.70	1,788	.036	532	Phase I	14.5
6/1	2,60	1.789	.037	446	Phase I	13.5
7/1	2,80	1,785	.035	480	Phase I	13.0

Table 1. PHYSICAL PROPERTIES OF PVF₂ FILMS AFTER STRETCHING*

*Films uniaxially stretched at 80 C

'Films poled at 500 kV/cm to 80 to 85 C in 45 minutes

Mixtures of Phase II and Phase 1

Infrared spectroscopy showed that the crystalline component of the PVF_2 film (as received) was predominantly in the phase II form,^{7,8} as evidenced by the presence of absorption bands at 615, 530, 410, 360, 290 cm⁻¹ (see Figure 1). As the degree of uniaxial stretching was increased in steps up to 5/1, the infrared spectra showed a continuous decrease in the 530 and 410 cm⁻¹ and a concomitant increase in the 445 cm⁻¹ band. These results indicate a gradual conversion of phase II to phase I due to the stretching process. At further increases in the draw ratio up to 7/1, no further changes were noted in the infrared spectra.

The increase in density of the PVF_2 film with stretching (see Table 1) may be attributed to the increased content of the higher density phase I form⁹ and may also result from an increase in the degree of crystallinity.

The increase in birefringence upon stretching, as noted in Table 1, is ascribed primarily to changes in degree of preferred orientation in the crystalline phase. The leveling off seen at the higher draw ratios suggests a saturation in the degree of crystalline orientation.

The change in the sonic modulus upon stretching, as noted in Table 1, is attributed primarily to changes in the amorphous regions of the polymer rather than in the crystalline regions. Unlike the birefringence, the sonic modulus continues to change at the higher draw ratios, indicating that the amorphous regions of the polymer continue to orient.



Figure 1. Infrared spectra of stretched PVF₂ films (from Reference 5).

- 7. CORTILI, G., and ZERBI, G. Chain Conformations of Polyvinylidene Fluoride as Derived from its Vibrational Spectrum. Spectrochim. Acta, v. 23A, 1967, p. 285.
- 8. ENOMOTO, S., KAWAI, Y., and SUGITA, M. Infrared Spectrum of Polyvinylidene Fluoride. J. Polym. Sci., v. 6, A-2, 1968, p. 861.
- 9. LANDO, J. B., OLF, H. G., and PETERLIN, A. Nuclear Magnetic Resonance and X-Ray Determination of the Structure of Polyvinylidene Fluoride. J. Polym. Sci., v. 4, A-1, 1966, p. 941.

The X-ray diffraction patterns seen in Figure 2 show that at low degrees of stretching the individual crystallites are randomly oriented. As the degree of stretching is increased, the crystallites assume an increasingly preferred orientation as indicated by the gradual breakup of the diffraction rings into spots. Also, the changes noticed in the diffraction spacings indicate a continuous conversion of phase II to phase I with increasing degree of stretching.

These results show that the effect of uniaxial stretching of PVF_2 is twofold: first, to produce a continuous conversion from crystalline phase II (tgtg') to phase I (planar zigzag) conformation; and second, to orient the crystalline and amorphous regions of the polymer.

Alternatively, biaxial stretching and also rolling processes were each investigated as a means of producing the desired film orientation without degradation of transverse film strength. The resultant physical and mechanical properties of the PVF_2 films are given in Table 2, along with the results of the uniaxial stretching for comparison.



26.44 RATE



Determination of the piezoelectric activity of the poled films gives results as typified in Figure 3. The curves are linear during the loading increments but become slightly nonlinear during the unloading increments. These results are quite reproducible after several loading and unloading cycles and are used to calculate the static piezoelectric constant.

With PVF_2 films poled under an effective field of 500 kV/cm, the static piezoelectric constant was found to vary with the prior draw ratio in the manner shown by Figure 4 and given in Table 1. The most rapid increase occurred between draw ratios of 3/1 and 5/1, paralleling the conversion of phase II crystalline conformation to phase I as a function of draw ratio. This suggested that the phase I crystalline material plays a considerable role in the piezoelectric behavior¹⁰ in

40. MURAYAMA, N. Piezoelectric and Pyroelectric Effects of Polymer Flectrets, Microsymposium on Electrical Properties of Polymers, Soc. Polym. Sci. Japan, Tokyo, Japan, January 1972.

	Orientation	Thickness	Birefringence	Sonic I	Modulus	Crystalline	P7 Constant*
Orientation	Ratio	(mils)	$(n_{\parallel} - n_{\perp})$	11	1	Conformation	(pcoul/nt)
Original		5,40	0.0045	336	376	Phase II	2.2
Uniaxial	5/1	2.70	.037	494	160	Phase I	12.5
Blaxial ⁺	3.8/1	1.50	.028	393	387	Phase I	11.0
kolled ⁺	3/1	2.00	.025	370	407	Phase I	7.0

Table 2. EFFFCTS OF DIFFERENT TYPES OF ORIENTATION ON THE $P^{*}_{1}YSICAL$ PROPERTIES OF PVF_2 FILMS

*Films poled at 500 kV/cm to 80 to 85 C in 1 hour

and the second secon

[†]Biaxial stretching and rolling to maximum amount attainable by these methods



addition to any effect produced by polymer orientation. The apparent leveling off of the piezoelectric constant at the high draw ratios agrees with our results that there is no further conversion of material to the phase I form and there is no further significant orientation of the crystalline regions at high draw ratios under these experimental conditions. The further increase of sonic modulus at the high draw ratios indicates that the continuing orientation of the amorphous material may contribute in only a minor way to the piezoelectric constant.

A comparison of the piezoelectric activity of PVF_2 films oriented by different processes but poled under similar conditions is given in Table 2. The highest values were obtained from the uniaxially and biaxially stretched samples, which have the greatest amount of polymer orientation and phase I crystalline conformation.

A series of experiments was run to determine the effects of the poling variables upon the subsequent piezoelectric activity of the uniaxially stretched PVF_2 films. The effect of the poling voltage upon the piezoelectric constant is shown in Figure 5, where one sees a smoothly rising curve which begins to level off at the higher voltages. When the highly stretched films were poled at fields of 500 kV/cm, but with variations in either the poling time or poling temperature, it was found that the piezoelectric activity increased at the low values of these variables but leveled off after poling times of 30 minutes and poling temperatures

、うても見ていないので



of 80 C. Longer poling times (up to 1-1/2 hours) and higher poling temperatures (100 to 110 C) had little effect on the piezoelectric activity.

It is evident that the orientation process is an important step in optimizing the piezoelectric effect in PVF₂. Stretching of this film, as previously mentioned, is a two-fold process; i.e., orientation of the polymer chains and conversion of crystalline chain conformation. We can investigate the influence of each contribution on the piezoelectric activity by using a PVF₂-TFE copolymer, which exists initially in the phase I form. The piezoelectric activity of the copolymer films that were poled under similar conditions as PVF_2 is given in Table 3. We see that the piezoelectric constant of the unoriented copolymer is higher than that of the unoriented PVF_2 . This indicates that the phase I crystalline conformation is the more active form. However, when the copolymer samples were uniaxially drawn, there was an increase in the piezoelectric constant. Thus we need not only the "right" crystalline form but also a certain degree of orientation in order to obtain the optimal piezoelectric effect.

Information about the effect of subsequent temperature conditioning on the piezoelectric activity of the stretched and poled PVF_2 films is needed before these polymer films can be incorporated as transducing elements in devices. The retention of the piezoelectric activity over a temperature range for a highly

ň

where the d and poled PVF_P film is plotted in Figure 6. Initial film activity was about 19 peoulombs/newton. With no field applied, the film was then reheated for one hour at the specified temperature before the piezoelectric activity was again determined at room temperature. It is seen that the piezoelectric activity was retained under these conditions up to 85 to 90 C, beyond which there was a continuous decrease with temperature. After subsequent temperature treatment to 150 C, about one half of the original activity was still retained.

A series of accelerated temperature aging experiments was run to determine the effect of increasing temperature upon the piezoelectric constant of PVF_2 . The poled films were placed between two metal electrodes, coupled to an electrometer, and inserted between the platens of a heated press. The piezoelectric constant was determined from room temperature to 150 C (upper curve) and back to room temperature (lower curve), as shown in Figure 7. The heating rate was 2 to 4 C per minute. The piezoelectric activity reached a maximum at 140 C and then dropped abruptly. The cooling portion of this test showed a permanent lowering of the piezoelectric constant.

Isothermal aging experiments were conducted in a similar manner except the temperature of each film was raised to a specified value and held constant for at least 100 hours. The piezoelectric constant was determined at this elevated temperature. As we can see from Figure 8, temperature treatments of 80 C have little

Uraw Ratio	Thickness (mils)	Density (g/cc)	Birefringence (n _{ll} - n _l)	Sonic Modulus (ksi)	Crystalline Conformation	PZ Constant† (pcoul/nt)
Orig.	6.5	1.88	0.0047	206	Phase I	7
1.9/1	3.6	1,88	.027	264	Phase I	9
2.5/1	4.0	1,88	.024	247	Phase I	9
3.6/1	3.4	1.88	.037	**	Phase I	16

Table 3. PHYSICAL PROPERTIES OF COPOLYMER PVF2-TFE FILMS AFTER STRETCHING*

*Copolymer films (27% TFE) uniaxially stretched at room temperature *Films poled at 500 kV/cm at 60 C in 45 minutes





の言語が法語の語言



Figure 8. Isothermal aging of poled PVF2.

8

effect on the piezoelectric activity for times up to 240 hours. When the temperature was 100 or 120 C, there was an initial rapid increase in piezoelectric constant, then a sharp decrease, followed by a more gradual decay. In each case there was a permanent decrease in the piezoelectric activity of the PVF_2 after the films were returned to room temperature at the conclusion of the experiment. For both the accelerated temperature and isothermal aging experiments, the apparent changes in piezoelectric constant may be influenced by factors such as changes in elastic modulus of the film with temperature, depolarization processes at the higher temperature, and pyroelectric effects.

Thus, for polymer films, the effect of subsequent temperature conditioning must be considered when these piezoelectric films are incorporated in devices. However, even with these temperature considerations, there are many applications for which piezoelectric polymer films can serve the Army.

We conducted a preliminary investigation of the dynamic piezoelectric behavior of poled PVF₂ films at room temperature. A typical value of the complex tensile piezoelectric strain constant, d_{31}^* was 26 pcoulombs/newton. This value remained essentially constant over a frequency ranging from 80 to 800 Hz. The phase angle between the polarization charge and the related force ranged from 0.4 to 1.2 degrees over this frequency span. A typical value of the corresponding complex tensile piezoelectric stress constant, e_{31}^* , was 4.6×10^6 pcoulombs/cm² over the same frequency span, with phase angles between polarization charge and displacement ranging from 1.6 to 2.2 degrees. The dynamic elastic modulus was about 1.8×10^{10} dynes/cm². The characterization of dynamic piezoelectric behavior of these PVF₂ films is an important step in the consideration of the films for Army application because of the dynamic nature of the events to be monitored.

APPLICATIONS

Through detailed characterization of polymer films and optimization of the orientation and polarization processes, we have been able to prepare PVF2 films with piezoelectric constants of 20 to 25 pcoul/nt. We now consider using these piezoelectric polymer films as transducing elements in devices because of the projected material advantages, such as low mass, sufficient flexibility to conform to irregular surfaces, resistance to mechanical shock, water resistance, ease and economics of fabrication. Our approach has been to fabricate several prototype devices in-house with these PVF_2 films to demonstrate their utility and potential advantages. Improvements in the design and fabrication of these and other prototype devices are currently being pursued through a joint effort between AMMRC and industrial contractors. This joint effort will provide an overall assessment of the advantages and disadvantages of specific transducer devices using piezoelectric polymer films. Descriptions, results from preliminary testing of these prototype devices, along with the Army applications, are now presented for the following specific devices: microphones, vibration sensors, strain gages, and medical sensors.

Microphones

The Army is interested in evaluating new types of sensor materials for microphones where improvements in shock and water resistance would offer distinct advantages over current dynamic microphones. A piezoelectric polymer microphone of

なるのである。

simple design was fabricated at AMMRC and demonstrated the above advantages. Improvements in the design and fabrication of this type of microphone resulted from work with two acoustic companies, each using PVF_2 films supplied by AMMRC. A noise-cancelling microphone, physically resembling the standard M-87 dynamic microphone was constructed by Thermo Electron Corporation (see Figure 9). This polymer microphone was bi-directional and had a flat frequency response up to 15 kHz. A ruggedized microphone was fabricated by Bolt, Beranek, and Newman (BBN) which demonstrated the following properties: good frequency response in the voice transmission region, high shock resistance, and ease of waterproofing. We are continuing our joint efforts with this latter company to further refine the design and fabrication of this microphone to be compatible for use with existing Army equipment. Subsequent evaluation and testing of this piezoelectric polymer microphone will be conducted by BBN and the Army Electronics Command (ECOM).

Vibration Sensors

The Army has need for on-condition vibration sensors to monitor stress and vibration levels in vehicular (air and ground) structures and power systems. Piezoelectric polymer transducers would offer advantages over conventional transducers owing to the low mass, nonbrittleness, flexibility, and ease of fabrication of the polymer sensor. We have fabricated some prototype vibration sensors at AMMRC and have demonstrated their ability to monitor vibrations. These flexible, lightweight accelerometers were mounted alongside a commercial accelerometer on a helicopter test gear box at Northrop Corporation. Figure 10 shows the output signals from both of these accelerometers collected at 4-minute intervals over a 20-minute time period. These preliminary results indicate that the polymer transducer had the capability of providing reasonably good diagnostic test data up to frequencies of 5.5 kHz for vibration amplitudes up to 70 g's.

We are currently involved in a joint effort with BBN to determine the potential use of piezoelectric polymers in transducers. Through a preliminary feasibility study, this company has fabricated a high shock resistance accelerometer



Figure 9. Comparison of microphones. M-87 dynamic microphone (top), plezoelectric polymer microphone (bottom).



Figure 10. Comparative amplitude – frequency response.

Piezoelectric polymer sensor

いてきましいましたのでしていたのであるので

معمد والرباد المربي الأربية

Commercial accelerometer

containing one of our PVF₂ films. Test results indicated a flat frequency response up to 20 kHz, transverse sensitivity of less than 3% maximum, output sensitivity of 0.2 mV/g, and a noise floor of 10 μ volts rms. We are encouraged by these results and we plan to continue joint efforts with this company to develop vibrational sensors of greater sensitivity.

Strain Gages

The Army is concerned with fatigue characteristics of materials used in structures because of the connection with, and prediction of, material failure. Strain gages are useful monitors of material deformation and hence offer means to indicate the onset of fatigue. Piezoelectric polymer films would be unique dynamic strain sensors owing to their flexibility and low modulus, the latter property providing sufficiently low mechanical impedance to be compatible with composite materials fabricated with low-modulus polymeric matrices. In a preliminary investigation at AMMRC we fabricated PVF₂ strain gages and mounted them on a fiber-reinforced plastic bar undergoing dynamic testing. The test machine applied dynamic strain levels of 0.5% peak-to-peak to the bar at frequencies of 10 to 30 Hz. A large stable output signal was produced by the PVF₂ film, showing wave shape, amplitude, and frequency of the resultant deformation in the test bar. Future work at AMMRC will be devoted to investigating the performance of PVF₂ film strain gages with regard to their strain magnitude limits, fatigue life, and useful operating temperatures.

Medical Sensors

Because piezoelectric polymer films are chemically inert, mechanically compliant, rugged, and a good impedance match to flesh, they are ideally suited for use in a variety of medical applications. For example, in a recent series of tests, Bolt, Beranek, and Newman (BBN) successfully demonstrated the use of PVF2 film as a transducing element in a simple, yet extremely effective pulse measurement device. Results of tests of peripheral pulse measurement using polymer film sensors are shown in Figure 11a, a photographic record of the pressure versus time observed at a fingertip. The sensor is a sheet of poled PVF_2 film which has been coupled to the fingertip with a lightweight holder designed for the purpose. Electronics have been built into the holder in order to eliminate spurious cable motion artifacts. The result is an extremely detailed display of dynamic blood pressure. The basic period of about 0.8 second is apparent, and pulse rate counting is clearly possible. In addition, there are remarkable similarities in detail between the observed waveform and arterial (aorta) blood pressure, as shown in Figure 11b.¹¹ The strength of the pulse is also evident, as is the decay rate of the pressure, and what appears to be a pronounced "dicrotic notch," which is associated with heart valve function. We conclude that polymer sensors can very conceivably play an important role in medicine; for example, measurement of pulse rate, strength, and rhythm during medical evacuation of wounded, cardiac monitoring during surgery, periodic examination and screening, monitoring of post operative patients, and intensive care monitoring as an adjunct to ECG. AMMRC and BBN are now cooperating on further development of medical devices employing piezoelectric polymer transducers.

^{11.} HURST, J. 'W., LOGUE, R. B., SCHLANT, R. C., and WENGER, N. K. The Heart Arteries and Veins. McGraw-Hill, New York, New York, 1974.



Figure 11a. Pressure waveform observed at the fingertip using a piezoelectric polymer sensor.



and the second second

Other Proposed Applications

The projected utility of piezoelectric polymers in a number of Army devices has been described by the foregoing examples of prototype development and testing. Other uses contemplated for piezoelectric polymers include applications involving ultrasonic transducers, ballistic impact detectors, counter-intrusion devices (both for combat and peacetime applications), hydrophones, and headphones. In addition, the phenomenon of pyroelectricity (electrical signal produced by temperature changes) is usually exhibited by piezoelectric polymers. Possible applications of pyroelectric polymer films include intrusion and fire detection, early detection of laser impact, and as large-area, shock-resistant sensing elements in infrared vidicons to depict thermal scenes at night.

FUTURE INVESTIGATIONS

In addition to the development and testing of prototype devices, we are pursuing efforts to extend the operating temperature of piezoelectric polymers through modifications in the structure of PVF_2 and/or through the development of other high temperature polymer systems. Presently, certain device applications employing piezoelectric PVF_2 polymers are limited by the loss of piezoelectric activity at elevated temperatures. We believe that our laboratory, with its considerable expertise in the field of polymers, can greatly contribute to future development of piezoelectric polymer materials leading to improved devices for Army applications.

12

DISTRIBUTION LIST

•

No. Copi	of es To
1	Office of the Director, Defense Research and Engineering, The Peatagon, Washington, D. C. 20301
12	Commander, Defense Documentation Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, Virginia 22314
1	Metals and Ceramics Information Center, Battelle Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201
2	Chief of Research and Development, Department of the Army, Washington, D. C. 20310 ATTN: Physical and Engineering Sciences Division
1	Commander, Army Research Office, P. O. Box 12211, Research Triangle Park, North Carolina 27709 ATTN: Information Processing Office
1	Commander, U. S. Army Materiel Development and Readiness Command, 5001 Eisenhower Avenue, Alexandria, Virginia 22333 ATTN: DRCLDC, Mr. R. Zentner
1 1	Commander, U. S. Army Electronics Command, Fort Monmouth, New Jersey 07703 ATTN: DRSEL-GG-DD DRSEL-GG-DM
1	Commander, U. S. Army Missile Command, Redstone Arsenal, Alabama 35809 ATTN: Technical Library DRSMI-RSM, Mr. E. J. Wheelahan
2	Commander, U. S. Army Armament Command, Rock Island, Illinois 61201 ATTN: Technical Library
1	Commander, U. S. Army Natick Research and Development Command, Natick, Massachusetts 01760 ATTN: Technical Library
1	Commander, U. S. Army Satellite Communications Agency, Fort Monmouth, New Jersey 07703 ATTN: Technical Document Center
2	Commander, U. S. Army Tank-Automotive Research and Development Command, Warren, Michigan 48090 ATTN: DRDTA, Research Library Branch
1	Commander, White Sands Missile Range, New Mexico 88002 ATTN: STEWS-WS-VT
1	Commander, Dugway Proving Ground, Dugway, Utah 84022 ATTN: Technical Library, Technical Information Division
1 1	Commander, Frankford Arsenal, Philadelphia, Pennsylvania 19137 ATTN: Library, H1300, Bl. 51-2 SARFA-L300, Mr. J. Corrie
1	Commander, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, Maryland 20783 ATTN: Technical Information Office
1 1	Commander, Picatinny Arsenal, Dover, New Jersey 07801 ATTN: SARPA-RT-S SARPA-FR-M-D, PLASTEC, A. M. Anzalone
4	Commander, Redstone Scientific Information Center, U. S. Army Missile Command, Redstone Arsenal, Alabama 35809 ATTN: DRSMI-RBLD, Document Section
1	Commander, Watervliet Arsenal, Watervliet, New York 12189 ATTN: SARWV-RDT, Technical Information Services Office
1	Commander, U. S. Army Foreign Science and Technology Center, 220 7th Street, N. E., Charlottesville, Virginia 22901 ATTN: DRXST-SD2

ana i

 $m_{\rm P}$

.)*:*>

o. (opie	es To
	Director, Eustis Directorate, U. S. Army Air Mobility Research and Development Laboratory, Fort Eustis, Virginia 23604 ATTN: Mr. J. Robinson, SAVDL-EU-SS
1	Librarian, U. S. Army Aviation School Library, Fort Rucker, Alabama 36360 ATTN: Building 5907
1	Commander, USACDC Air Defense Agency, Fort Bliss, Texas 79916 ATTN: Technical Library
1	Commander, U. S. Army Engineer School, Fort Belvoir, Virginia 22060 ATTN: Library
1	Commander, U. S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi 39180 ATTN: Research Center Library
1	Commander, U. S. Army Environmental Hygiene Agency, Edgewood Arsenal, Maryland 21010 ATTN: Chief, Library Branch
1	Commandant, U. S. Army Quartermaster School, Fort Lee, Virginia 23801 ATTN: Quartermaster School Library
1	Commander, U. S. Army Radio Propagaticn Agency, Fort Bragg, North Carolina 28307 ATTN: SCCR-2
1	Naval Research Laboratory, Washington, D. C. 20375 ATTN: Dr. J. M. Krafft - Code 8430
1	Chief of Naval Research, Arlington, Virginia 22217 ATTN: Code 471
2 1 1 1	Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433 ATTN: AFML/MXE/E. Morrissey AFML/LC AFML/LLP/D. M. Forney, Jr. AFML/MBC/Mr. Stanley Schulman
1 1	National Aeronautics and Space Administration, Washington, D. C. 20546 ATTN: Mr. B. G. Achhammer Mr. G. C. Deutsch - Code RR-1
1	National Aeronautics and Space Administration, Marshall Space Flight Center, Huntsville, Alabama 35812 ATTN: R-P&VE-M, R. J. Schwinghamer S&E-ME-MM, Mr. W. A. Wilson, Building 4720
1	Ship Research Committee, Maritime Transportation Research Board, National Research Council, 2101 Constitution Ave., N. W., Washington, D. C. 20418
1	Materials Sciences Corporation, Blue Bell Campus, Merion Towle Building, Blue Bell, Pennsylvania 19422
1	Masco Corporation, 21001 Van Born Road, Taylor, Michigan 48180
2 1 4	Director, Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172 ATTN: DRXMR-PL DRXMR-AG Authors

: : :

.

٤

.

1

.'

÷

ار میں بار ایک میں میں میں میں

.

Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172 PIEZOELECTRIC POLYMER FILMS FOR APPLICATION IN MONI-TORING DEVICES - Richard J. Shuford, Anthony F. Wilde, John J. Ricca, and George R. Thomas Technical Report AMMRC TR 77-2, February 1977, 16 pp illus-tables, D/A Project 111631020071, AMCMS Code 613102.12.15900

UNLINITED DISTRIBUTION Key Words Piezoelectricity Fluorocarbon

Polymer films

UNCLASSIFIED

B

To develop Army applications based on the pronounced piezoelectric effect noted for polyvinylidene Fluoride (PYr₂), our laboratory has conducted a systematic investigation of factors responsible for this remarkable behavior of an organic polymer. Commercial PYr₂ homopolymer films were oriented by uniaxial stretching, biaxial stretching, or rolling. The oriented films were characterized by means of infrared spectroscopy, density, birefringence, sonic modulus, and X-ray diffraction. The oriented films were then poled at various electric field strengths and temperatures for various times. Trends have been moted between draw ratio and the resulting physical properties; the piezoelectric activity has been correlated with draw ratio accelerated temperature aging and isothermal aging. Prototype devices have been folded at AWRK with these films for demonstrate their potential utility in microphones, vibration sensors, and strain gages. Further development efforts have been including a remarkable medical sensor. It is concluded that piezoelectric polymer films can provide unique and avantageous solutions to a number of Army problems requiring monitoring and communication devices.

Army Materials and Mechanics Research Center, Matertonn, Massachusetts 02172 PIEZOELECTRIC POLYMER FILMS FOR APPLICATION IN MONI-TORING DEVICES - Richard J. Shuford, Anthony F. Wilde, John J. Ricca, and George R. Thomas

B

Technical Report AWMRC TR 77-2, February 1977, 16 pp illus-tables, D/A Project 11153102D071, AMCMS Code 613102.12.15900

UNCLASSIFIED UNLIMITED DISTRIBUTION Key Words Piezoelectricity Fluorocarbon Polymer films

To develop Kingv applications based on the pronounced piezoelectric effect noted for polyvinylidene fluoride (PFz), our laboratory has conducted a systematic investigation of factors responsible for this remarkable behavior of an organic polymer. Commercial PVF_homopolymer and copolymer films were oriented by uniaxial structhing, infrared spectroscopy density, birefringence, sonic modulus, and X-ray diffraction. The oriented films were then poled at various electric field strengths and temperatures for various times. Trends have been noted between draw ratio and the resulting physical properties; the piezoelectric activity has been correlated with draw ratio accelerated temperature aging and isothermal aging. Prototype devices have been ricited at ANMAC with these films to demonstrate their potential utility in microphones, vibration sensors, and strain gages. Further development efforts have been ricited jointly with industrial firms to produce more refined prototype devices, including a remarkable medical sensor. It is concluded that piezoelectric polymer films can provide unique and advantageus solutions to a number of Army problems requiring monitoring and communication devices.

biarial stretching, or rolling. The oriented films were characterized by means of infrared spectroscopy, density, birefringence, sonic modulus, and X-ray diffraction. The oriented films were then poled at various electric field strengths and tempera-tures for various times. Trends have been noted between draw ratio and the resulting physical properties; the piezoelectric activity has been correlated with draw ratio UNLIMITED DISTRIBUTION Commercial PVF₂ homopolymer and copolymer films were oriented by uniaxial stretching, To develop Army applications based on the pronounced piezoelectric effect noted for pclyvinylidene fluoride (PVF₂), our laboratory has conducted a systematic investigation of factors responsible for this remarkable behavior of an organic polymer. Any polying conditions. The preconcurrently may also been investigated after accelerated temperature aging and isothermal aging. Prototype devices have been fab-ricated at AWRC with these films to demonstrate their potential utility in micro-phones, vibration sensors, and strain gages. Further development efforts have been conducted jointly with industrial firms to produce more refined prototype devices, including a remarkable medical sensor. It is concluded that piezoelectric polymer films can provide unique and advantageous solutions to a number of Army problems requiring monitoring and communication devices. Prototype devices have been fab-Piezoelectricity UNCLASSIFIED Polymer films Key Words Fluorocarbon ð Shuford, Anthony F. Wilde, Watertowm, Massachusetts 02172 PIEZOELECTRIC POLYMER FILMS FOR APPLICATION IN MONI-Technical Report ANMRC TR 77-2, February 1977, 16 pp illus-tables, D/A Project 11163102D071, AMCMS Code 613102.12.15900 Materials and Mechanics Research Center, TORING DEVICES — Richard J. Shuford, John J. Ricca, and George R. Thomas Army

Army Materials and Mechanics Research Center, Army Materials and Mechanics Research Center, Materials and Mechanics Research Center, PIEZOBELECTRIC POLYMER FILMS FOR APPLICATION IN MONI-TORING DEVICES - Richard J. Shuford, Anthony F. Wilde, John J. Ricca, and George R. Thomas

John J. Ricca, and George R. Thomas Technical Report AMMRC TR 77-2, February 1977, 16 pp -illus-tables, D/A Project 11163102D071, AMCMS Code 613102.12.15900

Piezoelectricity Fluorocarbon Polymer films

UNLIMITED DISTRIBUTION

Key Words

UNCLASSIFIED

80

To develop Army applications based on the pronounced piezoelectric effect noted for polyvinylidene fluoride (PVF₂), our laboratory has conducted a systematic investigation of factors responsible for this remarkable behavior of an organic polymer. Commercial PVF₂ homoplymer and copolymer films were oriented by uniaxial stretching, plaxial stretching, or rolling. The oriented films were characterized by means of infrared spectroscopy, density, birefringence, sonic modulus, and X-ray diffraction. The oriented films were then poled at various electric field strengths and temperatures for various times. Trends have been noted between draw ratio and the resulting physical properties; the piezoelectric activity has also been investigated after accelerated temperature aging and isothermal aging. Prototype devices have been fabphoses, vibration sensors, and strain gages. Further development efforts have been conducted jointly with industrial firms to produce more refined prototype devices, including a remarkable medical sensor. It is concluded that piezoelectric so including a remarkable medical sensor. It is concluded that piezoelectric so including a remarkable medical sensor. It is concluded that piezoelectric so including a remarkable medical sensor. It is concluded that piezoelectric solven including a remarkable medical sensor. It is concluded that precolectines, including a remarkable medical sensor solutions to a number of Army problems requiring monitoring and communication devices.

biaxial stretching, or rolling. The oriented films were characterized by means of infrared spectroscopy, density, birefringence, sonic modulus, and X-ray diffraction. The oriented films were then poled at various electric field strengths and tempera-tures for various times. Trends have been noted between draw ratio and the resulting physical properties; the piezoelectric activity has been correlated with draw ratio and poling conditions. The piezoelectric activity has been correlated with draw ratio and poling conditions. The piezoelectric activity has also been investigated after accelerated temperature aging and isothermal aging. Prototype devices have been fab-ricated at AMRC with these films to demonstrate their potential utility in micro-phones, vibration sensors, and strain gages. Further development efforts have been conducted jointly with industrial firms to produce more refined prototype devices, including a remarkable medical sensor. It is concluded that piezoelectric polymer films can provide unique and advantageous solutions to a number of Army problems requiring monitoring and communication devices. To develop Army applications based on the pronounced piezoelectric effect noted for polyvinylidene fluoride (PVF_2), our laboratory has conducted a systematic investiga-tion of factors responsible for this remarkable behavior of an organic polymer. Commercial PVF_2 homopolymer and copolymer films were oriented by uniaxial stretching, finarial stretching, or rolling. The oriented films were characterized by means of infrared spectroscopy, density, birefingence, sonic modulus, and X-ray diffraction, the oriented films were then poled at various electric field strengths and tempera-tures for various times. Trends have been noted between draw ratio and the resulting physical properties; the piezoelectric activity has been correlated with draw ratio and poling conditions. The piscoelectric activity has also been investigated after accelerated temperature aging and isothermal aging. Prototype devices have been fab-ricated at AMENC with these films to demonstrate their potential utility in micro-UNLIMITED DISTRIBUTION UNLIMITED DISTRIBUTION To develop Army applications based on the pronounced piezoelectric effect noted for polyvinylidene fluoride (PVF_2), our laboratory has conducted a systematic investigation of factors responsible for this remarkable behavior of an organic polymer. Commercial PVF_2 homopolymer and copolymer films were oriented by uniaxial stretching, phones, vibration sensors, and strain gages. Further development efforts have been conducted jointly with industrial firms to produce more refined prototype devices, including a remarkable medical sensor. It is concluded that piezoelectric polymer. **Piezoelectricity Piezoelectricity** UNCLASSIFIED UNCLASSIFIED films can provide unique and advantageous solutions to a number of Army problems requiring monitoring and communication devices. Polymer films Polymer films Key Words Fluorocarbon Key Words Fluorocarbon P P Å0 TORING DEVICES - Richard J. Shuford, Anthony F. Wilde, John J. Ricca, and George R. Thomas Shuford, Anthony F. Wilde, Watertowm, Massachusetts 02172 PIEZOELECTRIC POLYMER FILMS FOR APPLICATION IN MONI-TORING DEVICES - Richard J. Shuford, Anthony F. Wilds Watertown, Massachusetts 02172 PiEZOELECTRIC POLYMER FILMS FOR APPLICATION IN MONI-Technical Report AWWRC TR 77-2, February 1977, 16 pp --illus-tables, D/A Project 17163102D071, AMCMS Code 613102,12,15900 Technical Report AMMRC TR 77-2, February 1977, 16 pp -illus-tables, D/A Project 11163102D071, AMCMS Code 613102.12.15900 Army Materials and Mechanics Research Center, Materials and Mechanics Research Center, John J. Ricca, and George R. Thomas Area polyvinylidene fluoride (PF2), our laboratory has conducted a systematic investiga-tion of factors responsible for this remarkable behavior of an organic polymer. Commercial PVF2, homopolymer films were oriented by uniaxial stretching, hiaxial stretching, or rolling. The oriented films were characterized by means of infrared spectroscopy, density, birreringence, sonic modulus, and X-ray diffraction. The oriented films were then poled at various electric field strengths and tempera-tures for various times. Trends have been noted between draw ratio and the resulting physical properties; the piezoelectric activity has also been investigated after accelerated temperature aging and isothermal aging. Prototype devices have been fonces, vibration sensors, and strain gages. Further development efforts have been conducted jointly with industrial firms to demonstrate their potential utility in micro-phones, vibration sensors, and strain gages. Inther development efforts have been including a remarkable redical sensor. It is concluded that piezoelectric polymer firms can provide undestrial sensor. It is concluded that piezoelectric polymer firms can provide undestrial sensor. It is concluded that piezoelectric polymer firms can provide undestrial sensor. It is concluded that piezoelectric polymer firms can provide undestrial sensor. tures for various times. Trends have been noted between draw ratio and the resulting physical properties; the piezoelectric activity has been correlated with draw ratio and poling conditions. The piezoelectric activity has also been investigated after accelerated temperature aging and isothermal aging. Prototype devices have been fab-ricated at MMRC with these ims to demonstrate their potential utility in micro-UNLIMITED DISTRIBUTION polyvinylidene fluoride (PVr.), our laboratory has conducted a systematic investiga-tion of factors responsible for this remarkable behavior of an organic polymer. Commercial PVF, homopolymer and copolymer films were oriented by uniaxial stretching, biaxial stretching, or rolling. The oriented films were characterized by means of referred spectroscopy, density, birefringence, sonic modulus, and X-ray diffraction. The oriented films were then poled at various electric field strengths and tempera-UNLIMITED DISTRIBUTION pnones, vibration sensors, and strain gages. Further development efforts have been conducted jointly with industrial firms to produce more refined prototype devices, including a remarkable medical sensor. It is concluded that piezoelectric polymer films can provide unique and advantageous solutions to a number of Army problems requiring monitoring and communication devices. ic develop Army applications based on the pronounced piezoelectric effect noted for To develop Army applications based on the pronounced piezoelectric effect noted for **Piezoeiectricity Piezoelectricity** UNCLASSIFIED UNCLASSIFIED Polymer films Polymer films Key Words Fluoroce-bon Fluorocarbon Key Words Å 8 • Watertown, Massachusetts 02172 PIEZOELECTRIC POLYMER FILMS FOR APPLICATION IN MONI-TORING DEVICES - Richard J. Shuford, Anthony F. Wilde, TORING DEVICES - Richard J. Shuford, Anthony F. Wilde, Hatertown, Massachusetts 02172 Piccoelectric POLYMER Films FOR APPLICATION IN MONI-Technical Report AMMRC TR 77-2, February 1977, 16 pp -"lius-tab"es, D/A Project ITI631020071, AMCMS Code 613102.12.15900 Technical Report AMMRC TR 77-2, February 1977, 16 pp illus-tables, D/A Project 11163102D071, AMCMS Code 613102.12.15900 requiring monitoring and communication devices. Materials and Mechanics Research Center, Materials and Mechanics Research Center, Jonn J. Ricca, and George R. Thomas John J. Ricca, and George R. Thomas

Activ

Army