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EVALUATION OF A P(VDF-TrFE) COPOLYMER WITH FLEXIBLE ELECTRODES MANUFACTURED BY AMP SENSORS LTD.

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Abstract

The ferroelectric copolymer poly(vinylidene difluoride- trifluoroethylene) shows considerable promise as a transducer material for sonar transducers. This material has a low density, is flexible and has a hydrostatic figure of merit which can be an order of magnitude better than that of lead zirconate titanate which is currently the most commonly used transducer material. We have investigated a 0.500 mm thick copolymer with thin flexible aluminium coated nickel electrodes manufactured by AMP Sensors Ltd of the USA. We have determined the elastic, dielectric, piezoelectric and hydrostatic properties of the copolymer with the flexible electrodes. The hydrostatic voltage coefficient and the hydrostatic figure of merit of this copolymer sample are at least five times better than those of lead zirconate titanate but they are not as good as values for the same copolymer with stiff electrodes which were investigated earlier. These properties have a small dependence on pressure and in this regard the present material is better than other polymers studied earlier.

Résumé

Le copolymère de bifluoride de vinylidène avec le trifluoroethylène est un matériau ferroélectrique qui se révèle prometteur comme matériau pour les transducteurs de sonar. Ce matériau a une faible masse volumique, il est flexible et son facteur de mérite hydrostatique peut être de l'ordre de dix fois mieux que celui du zirconate -titanate de plomb qui est courammant le matériau le plus utilisé dans les transducteurs. Nous avons examiné une feuille, de 0,500 mm d'épaisseur, d'un copolymère, muni des électrodes minces et fléxibles du nickel plaqué de l'aluminium, qui est fabriqué par AMP Sensors Ltd des Etats Unis. Nous avons déterminés les constantes élastiques, diélectriques, piézoélectriques et hydrostatiques de l'échantillon de copolymère muni de ces électrodes fléxibles. Le coefficient hydrostatique de tension et le facteur de mérite hydrostatique de ce matériau sont au moins cinq fois mieux que ceux du zirconate -titanate de plomb mais ils ne sont pas aussi bons que les coefficients du même copolymère muni des électrodes rigides que nous avons caractérisé avant. Ces propriétés ont une petite dépendance sur la pression hydrostatique mais cette dépendance est plus faible que celle trouvée pour des polymères étudiés auparavant.

1. INTRODUCTION

Polyvinylidene difluoride (PVDF) is a piezoelectric polymer which offers some advantages over lead zirconate titanate (PZT) as the sensor material of choice for use in sonar transducers. Its advantages include mechanical flexibility, good acoustic impedance matching to water, low cost and ease of construction. The piezoelectric and pyroelectric properties of PVDF are somewhat enhanced if the vinylidene fluoride is copolymerised with trifluoroethylene (TrFE) which appears to make it easier for chains to rotate in the vinylidene fluoride. Sometimes a proper distinction is not made between the copolymer and PVDF and the latter term has been used to describe both materials.

A proprietory commercial copolymer material is manufactured by AMP Sensors Ltd. of Valley Forge, Pennsylvania, USA. The material is initially made in layers of 0.500 mm thickness and up to 5" x 7" (0.127 m x0.178 m) in area. However thicker tiles can be obtained by laminating the material with or without interleaving electrodes corresponding to their P and S series of product classification respectively. A six inch square sheet of the 0.500 mm copolymer with a flexible electrode of aluminum over nickel was supplied to us by Mr. Mitch Thompson of AMP Sensors Ltd. and this report presents our characterisation of this sample.

It should be noted that, since the copolymer material has a low density and is soft, the effect of the electrodes on its mechanical properties is significant. We have also received samples of copolymer with stiff electrodes from the same company and our characterisation of this material is the subject of a separate report[1].

2. MEASUREMENTS

2.1 Specimens

The copolymer sample supplied to us was in the form of a six inch (15.2 cm) square sheet of 0.5 mm thickness with thin flexible electrodes of aluminium coated nickel. From this sheet, five one inch squares were cut and these were used for characterising the material.

2.2 Material Constants from Resonance Measurements

Impedance spectra of the samples were analysed using Smits' method[2] which has been outlined in an earlier report[3]. We have analysed the thickness extensional resonances of the specimens to determine the real and imaginary components of the mechanical stiffness at constant dielectric displacement c_{33}^{D}, the dielectric constant at constant strain ε_{33}^{S}, the piezoelectric coefficient in the poling direction h_{33}, and the thickness mode electromechanical coupling factor k_t. In Table 1 we give the averages of our results on the five specimens. Variations between the samples were between 3% and 10% with the exception of the imaginary part of the dielectric constant ε_{33}^{S}, which had a variation of up to 28%. In Figure 1 we show the sample impedance scans along with the theoretical fits obtained by using the material constants calculated for the specimen.

Table 1: Average thickness-extensional material constants

Property	Value
c_{33}^{D} (10^9 N/m^2)	6.46(1+0.032i)
ε_{33}^{S} (10^{-11}F/m)	3.68(1+0.158i)
h_{33} (10^9V/m)	3.25(1+0.130i)
k_t	0.244(1+0.193i)

In comparison with the values found for the copolymer tiles with stiff electrodes[1], the values of c_{33}^{D} and h_{33} for this flexible copolymer are higher by factors of about 4 and 2 respectively, the value of the imaginary part of k_t is almost 4 times larger whereas that of ε_{33}^{S} is somewhat smaller. These differences are caused by the fact that the stiff electrodes are thicker and increase the mass of the electrode-polymer composite; this effect is consistent with earlier observations in the case of PVDF samples obtained from the RAYTHEON company[4].

An attempt was made to study the thickness length resonance in the copolymer and to study the effects of varying the aspect ratio (defined as the length divided by the width) of the specimens. Tiles of the copolymer were cut in 6.0 cm lengths, with aspect ratios of 10 and 20. These tiles were cut with their lengths both parallel and perpendicular to a chosen edge of the supplied sheet in order to check possible anisotropy in the 1 and 2 directions which might have been caused by stretching or other processes during production of the material. The presence of anisotropy would cause different levels of resonance peaks in the samples cut in different directions. However, the length resonance peaks could not be detected in the impedance scans and hence no conclusions could be drawn about the material constants governing these resonances. The absence of the resonance peaks is likely to be due to the clamping effects of the electrodes on the soft copolymer samples.

2.3 The Low Frequency Dielectric Constant

The low frequency capacitances of the samples were measured at a frequency of 400 Hz with the help of a Hewlett Packard 4192A Impedance Analyser and the results were used to find the average low frequency permittivity and the average dielectric constant of the material:

$$\varepsilon_{33}^{T} = 6.71\times10^{-11} \pm 1\%\ \text{F/m} \qquad \text{and} \qquad \frac{\varepsilon_{33}^{T}}{\varepsilon_o} = 7.58 \pm 1\% \ .$$

The low frequency dissipation was found to be less than 2%. Our results on the permittivity and the dissipation agree well with our earlier measurements on the AMP copolymer tiles with the stiff

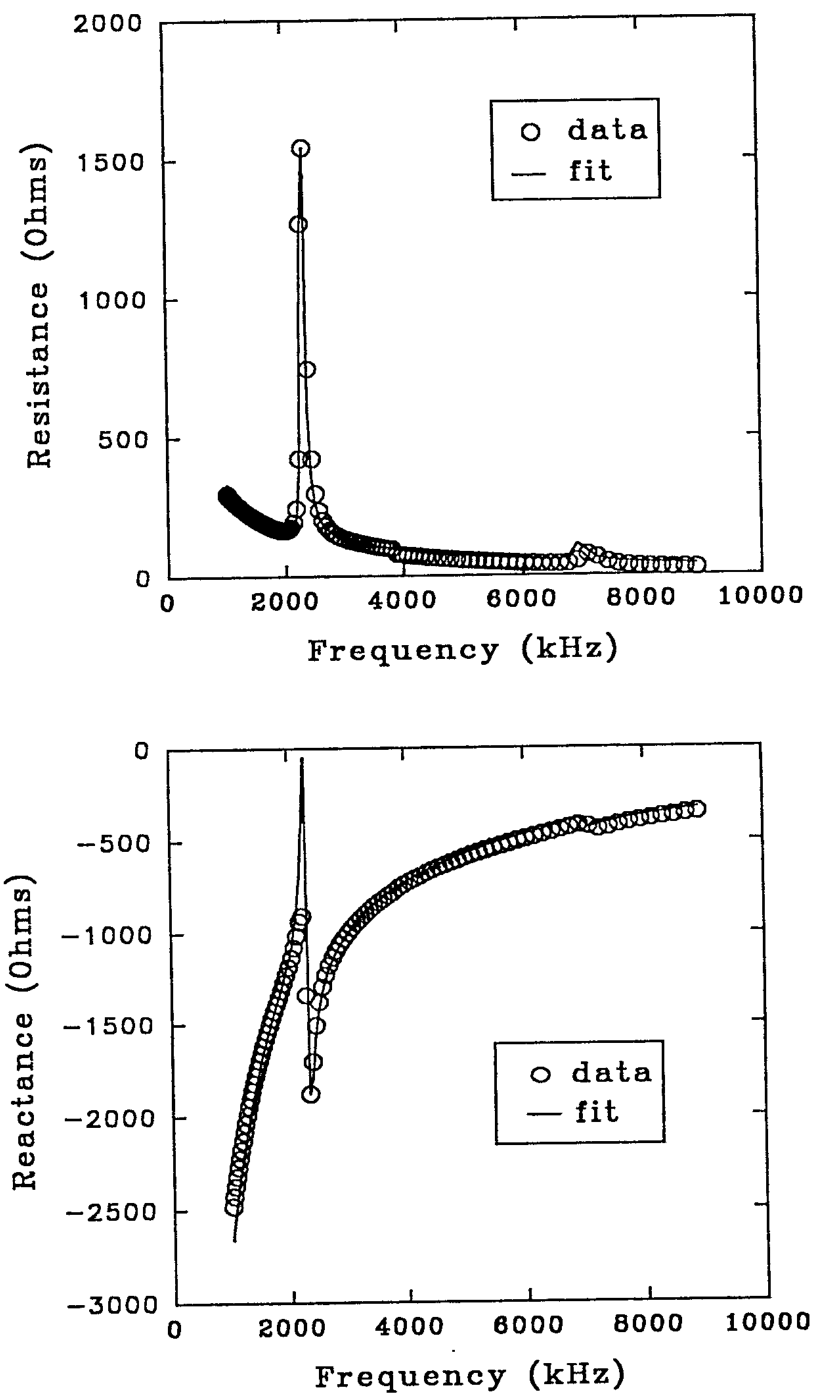

Figure 1. The real and imaginary parts of a typical frequency spectrum of the thickness-extensional resonance of a poled copolymer sample. The measurements were carried out at 22°C. The points represent measurements and the line is the fit obtained by using the material constants determined from the measurements.

electrodes[1] and with measurements by Wang et al on similar clamped copolymer tiles[5].

2.4 Measurement of the Piezoelectric Charge Constant in the 33 Direction

The value of d_{33} was obtained using a 1 cm^2 force head on a Berlincourt type meter which was operated at a frequency of 200 Hz. Table 2 shows values of d_{33} for our five samples of copolymer. These results yield an overall average value of 29 ± 12% pC/Nwhich may be compared with the value of 24.75 pC/N found by Wang et al[5].

Table 2: Measured values of d_{33} for the five samples

sample	1	2	3	4	5
d_{33} (pC/N)	27.2	30.6	31.0	29.4	26.7

2.5 Hydrostatic Measurements

The hydrostatic voltage coefficient, g_h, was measured as a function of pressure at a temperature of 20° C using a frequency of 400 Hz. The hydrostatic figure of merit which is the product of the hydrostatic voltage and charge coefficients is given by $g_h d_h = g_h^2 \varepsilon_{33}^T$. Table 3 gives the average values of both the hydrostatic voltage coefficient and the hydrostatic figure of merit for pressures between 2 MPa and 14 MPa while figures 2 and 3 show the variation of these quantities as a function of pressure.

Table 3: Average hydrostatic coefficients

pressure (MPa)	g_h (10^{-3}Vm/N)	$g_h\ d_h$ ($10^{-15}Pa^{-1}$)
2	140 ± 3%	1310 ± 6%
4	134 ± 3%	1200 ± 6%
6	132 ± 3%	1170 ± 6%
8	130 ±2%	1130 ± 4%
10	129 ± 2%	1110 ± 4%
12	128 ± 2%	1100 ± 4%
14	127 ± 2%	1080 ± 4%

We note that both the hydrostatic voltage coefficient and the figure of merit decrease as a function of pressure. As between pressures of 2 MPa and 14 MPa, the hydrostatic voltage coefficient decreases by

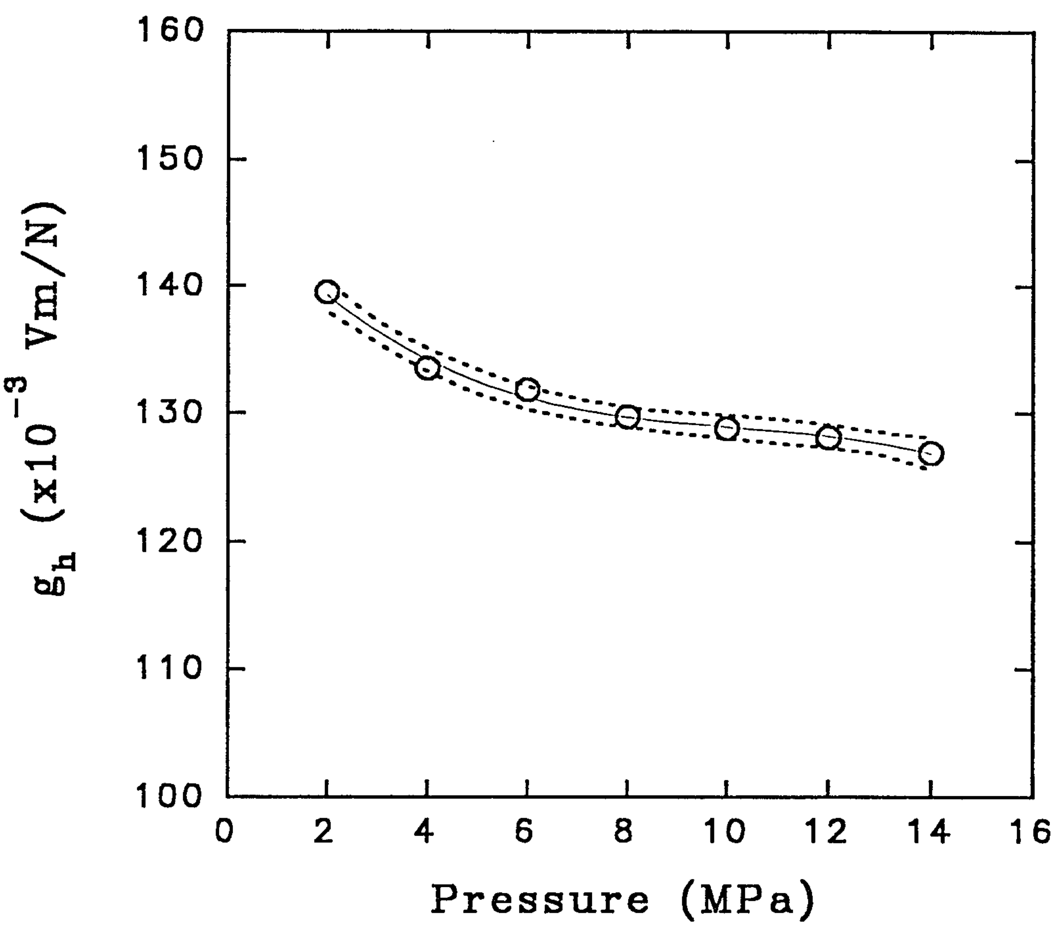

Figure 2. The pressure dependence of the average hydrostatic voltage coefficient, g_h, of the copolymer showing data and the polynomial fit to the data with the 95% confidence limits shown as dotted lines.

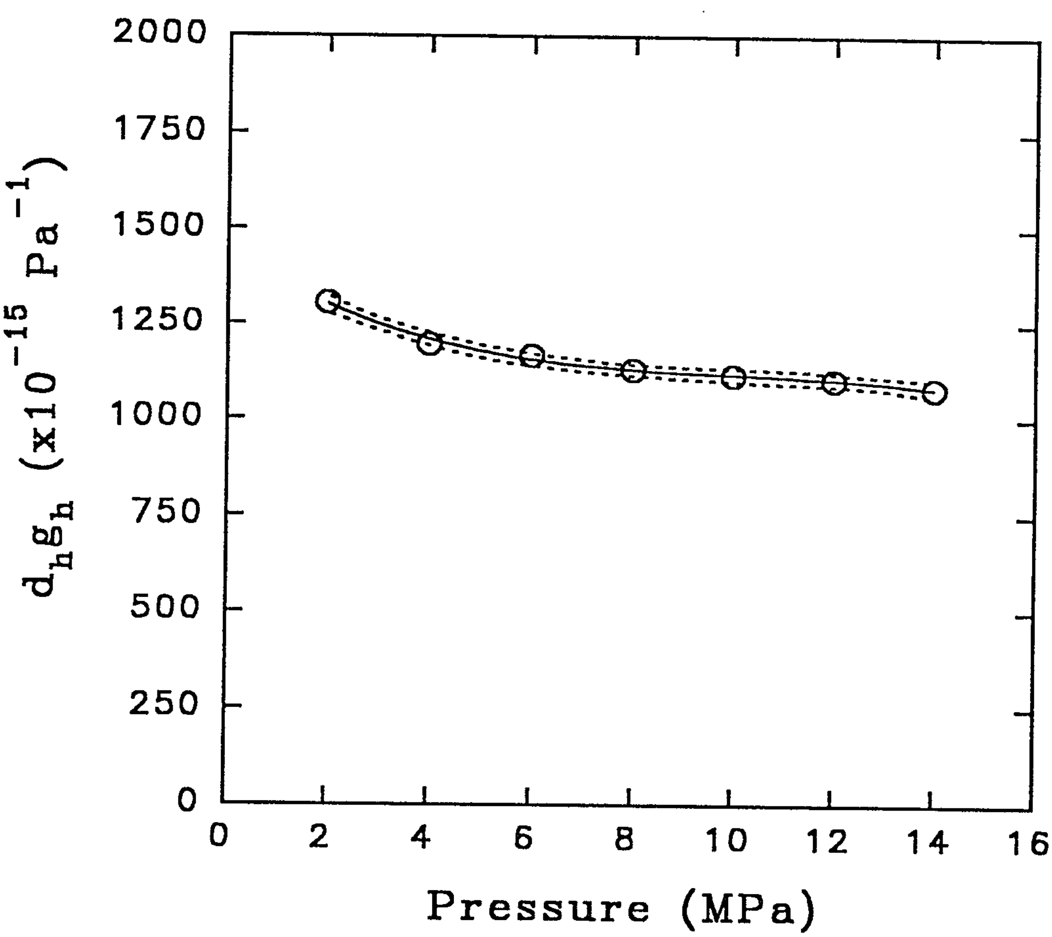

Figure 3. The pressure dependence of the average figure of merit, $g_h d_h$, of the copolymer showing data and the polynomial fit to the data with the 95% confidence limits shown as dotted lines.

around 9% and the figure of merit decreases by about 17% and these values are not very different from the values which we obtained for the copolymer with thick electrodes[1]. The variation could be fit by polynomials as follows:

$$g_h = a_3P^3 + a_2P^2 + a_1P + a_0$$

with

a_0 = 147.24 (10^{-3} Vm/N), a_1 = -4.808 (10^{-3} Vm/(N(Mpa))

a_2 = 0.4435 (10^{-3} Vm/(N(MPa)^2), a_3 = -0.0114583 (10^{-3} Vm/(N(MPa)^3)

and

$$d_hg_h = b_3P^3 + b_2P^2 + b_1P + b_0$$

with

b_0 = 1447.7(10^{-15}Pa^{-1}), b_1 = -88.440(10^{-15}Pa^{-1})/(MPa)

b_2 = 8.2274(10^{-15}Pa^{-1})/(MPa)^2, b_3 = -0.27083,(10^{-15}Pa^{-1})/(MPa)^3

where P is the pressure in MPa, g_h is in 10^{-3}Vm/N and g_hd_h is in 10^{-15}Pa^{-1}. The fits of these polynomials to the data are shown in figures 2 and 3 which also show the 95% confidence curves for the polynomials.

3. CONCLUSIONS

We have characterised the dielectric, piezoelectric and hydrostatic properties of 0.500 mm thick P(VDF-TrFE) copolymer with flexible electrodes manufactured by AMP Sensors Ltd. The hydrostatic coefficients are at least a factor of 5 better than those of lead zirconate titanate (PZT). However these coefficients show a small decrease as a function of pressure and they are not as good as the hydrostatic properties of a similar copolymer with stiff electrodes. Purely on the basis of their hydrostatic properties, it would appear that the S series copolymer with thick electrodes, on which we have reported earlier[1], is the better material for use in sonar transducers.

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