PVDF복소수 탄성, 유전, 압전 상수 측정

Measurement of All the Material Constants of PVDF

노 용 래*

(Yongrae Roh*)

요 약

압전 복합체 PVDF의 복소수 탄성, 유전, 압전 상수를 측정하였다. 사용된 방법은 각각 초음파 투과법, 임피던스 분석법, 탄성표면파 측정을 통한 수치해석을 이용하였고, 측정치중 일부는 이미 보고된 값들과 비교해보았다. 측정치의 신뢰성 증명을 위해 동일 기법을 압전 세라믹 PZT-5H에 적용해 검증하였다.

ABSTRACT

PVDF, a piezoelectric material, finds many applications since it is the only piezoelectric material in polymer form as opposed to conventional piezoceramics. However, its properties are not well characterized due to the avalilability of poled PVDF only as a thin film. Uniaxially oriented poled PVDF is of orthorhombic mm2 symmetry. All nine complex elastic constants, three complex dielectric constants as well as five complex piezoelectric constants are presented using a thin film and stacked cubical samples of uniaxially oriented poled PVDF film. Ultrasonic measurements, an impedance analyzer and a least square fitting technique are used to obtain the measured data.

I. Introduction

During the last decade, the piezoelectric polymer, PVDF(polyvinylidene fluoride), has become increasingly important as a transducer material, combining mechanical ruggedness, flexibility and chemical inertness with high piezoelectric response and useful acoustic properties. Applications include microphones, medical diagnostic transducers and towed sonar arrays[1]. Experimental and theoretical work concerning the piezoelectric properties of PVDF films has been reported by many investigators, such as D. Ricketts, R.E.Newnham, and E.L.Nix [2-4]. But it is surprising that, in spite of the extensive studies done on PVDF, all the material properties such as the elastic, dielectric and piezoelectric constants are not yet available. One of the reasons is the availability of poled PVDF only as a thin film. In designing various piezoelectric sensors, transducers, surface acoustic wave(SAW) devices, especially for the numerical simulation of their performance when exposed to various environments, all their material properties need to be known. Hence, there is much interest in the measurement of the material properties of

* 산업과학기술연구소

PVDF.

This paper reports all the complex, frequency dependent elastic, dielectric and piezoelectric properties of a voided form of PVDF which is poled to the uniaxial stretch direction (poled in the thickness direction). For all nine complex elastic stiffness constants (at constant electric displacement field D), a bulk wave through-transmission method is employed. The advantage of using this technique is that, compared with other methods, it is very simple and gives accurate results. For all three complex dielectric constants (at constant stress T), an impedance analyzer is used. For the measurement of the complex elastic and dielectric constants, two cubical samples of stacked PVDF film are prepared. For all five complex piezoelectric constants, a numerical least square method is used to fit optimally the material constants to a complex SAW wave number measured with a low frequency SAW device. This technique has such advantages as that frequency is easily controlled by changing the inter-digital electrodes (IDTs) of the SAW device, at least four piezoelectric constants of the five are obtained simultaneously from one measurement and accuracy is good[5]. To check the validity and accuracy of the measurement techniques, the same techniques are applied to PZT-5H and the results are compared with known values.

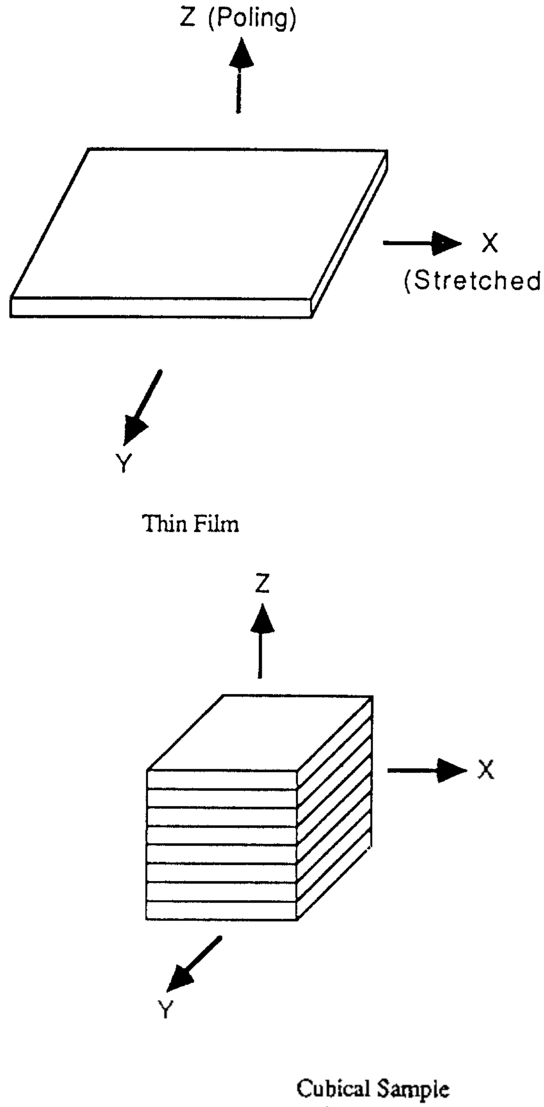

Fig. 1. Reference Axes of PVDF

II. Relationship Between Elastic Constants and Bulk Wave Rropagation in PVDF

Stretched and uniaxially oriented poled PVDF films have orthorhombic mm2 symmetry and the matrix of elastic stiffness constants has nine independent terms. The reference X axis is parallel to the film stretch direction, and the Z axis is perpendicular to the film surface as shown in Fig. 1. For the stiffness constants, the bulk wave through-transmission technique is employed, which can give both the bulk wave velocity v and the attenuation coefficient α of a sample from one single measurement of the amplitude and phase of the transmitted signal. For the diagonal elements of the stiffness matrix, normally incident waves are launched, while for the non-diagonal elements, obliquely incident waves are launched. Figure 2 shows the general view of the measurement, for both normal and oblique incidence. First, with just a delay line, the reference data such as delay time,

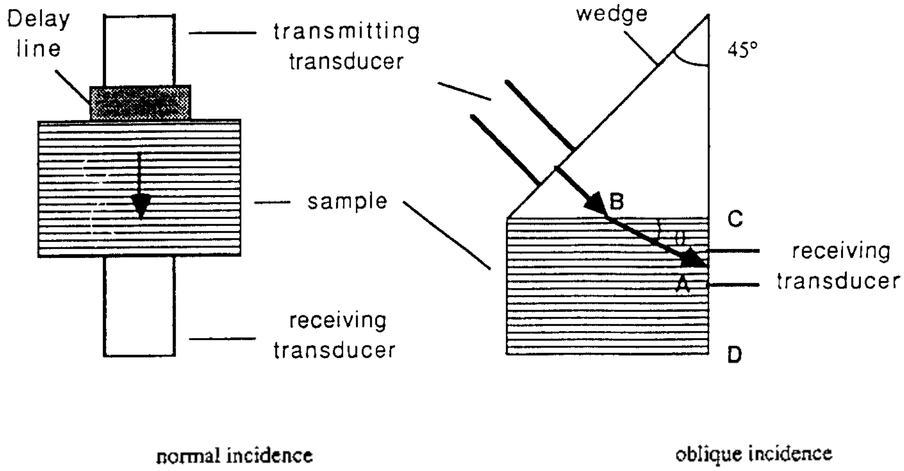

Fig. 2. General View of Elastic Stiffness Constant Measurement

phase and magnitude spectrum of the signals are taken. Based on these data, the sampling delay time of the wave for a sample is measured in the time domain. Using the FFT technique, in the frequency domain, the phase and the magnitude of each frequency component of the wave are obtained. With these results, the phase velocity of the wave in the PVDF sample is calculated as

$$v = \Delta d / [\Delta t + \Delta\phi / 2\pi f] \quad \text{(m/sec)} \tag{1}$$

and the attenuation coefficient is

$$\alpha = \Delta M / \Delta d \quad \text{(dB/m)} \tag{2}$$

where Δd is the travel distance of the wave, i.e. the length of the sample, Δt is the delay time of sampling the signals, $\Delta\phi$ and ΔM are the phase and the magnitude difference of the spectrum of the signals, and f is the frequency. From the phase velocity and attenuation coefficient, a complex wave number is calculated as[6]

$$k = \omega / v + i(\alpha \ln_e 10) / 20 \tag{3}$$

Based on this idea, C_{11}, C_{22}, and C_{33} are obtained directly by measuring the wave numbers k_{11}, k_{22}, and k_{33} by launching normally incident P waves alog the principal material axes.

$$C_{11} = \rho(\omega / k_{11})^2 \tag{4}$$

$$C_{22} = \rho(\omega / k_{22})^2 \tag{5}$$

$$C_{33} = \rho(\omega / k_{33})^2 \tag{6}$$

Similarly, C_{44}, C_{55} and C_{66} are obtained by the normal incidence of appropriately polarized S waves along the principal material axes. They are

$$C_{44} = \rho(\omega / k_{44})^2 \tag{7}$$

$$C_{55} = \rho(\omega / k_{55})^2 \tag{8}$$

$$C_{66} = \rho(\omega / k_{66})^2 \tag{9}$$

For the measurement of the non-diagonal terms C_{12}, C_{13} and C_{23}, obliliquely incident, either, longitudinal or transverse, waves are needed to be launched on the material XY, XZ and YZ planes, respectively. As seen in Fig.2, when the incident waves are launched at a certain angle, they go through the sample at another angle θ according to the Snell's law. The wave velocity in the plane is given as a function of this angle θ. If longitudinal waves are used, for the material XY, XZ and YZ planes, C_{12}, C_{13} and C_{23} are determined for the particular angle θ from the following equations[4]

$$(k_{12}/\omega) = (2\rho)^{\frac{1}{2}}\left[C_{66}+C_{11}\cos^2\theta + C_{22}\sin^2\theta + \sqrt{(C_{66}+C_{11}\cos^2\theta + C_{22}\sin^2\theta)^2 - 4B}\ \right]^{\frac{-1}{2}}$$

$$B = (C_{11}\cos^2\theta + C_{66}\sin^2\theta)(C_{66}\cos^2\theta + C_{22}\sin^2\theta) - (C_{12}+C_{66})^2\cos^2\theta\sin^2\theta \qquad (\theta \text{ from X axis}) \tag{10}$$

$$(k_{13}/\omega) = (2\rho)^{\frac{1}{2}}\left[C_{55}+C_{33}\cos^2\theta + C_{11}\sin^2\theta + \sqrt{(C_{55}+C_{33}\cos^2\theta + C_{11}\sin^2\theta)^2 - 4\overline{B}}\ \right]^{\frac{-1}{2}}$$

$$\overline{B} = (C_{55}\cos^2\theta + C_{11}\sin^2\theta)(C_{33}\cos^2\theta + C_{55}\sin^2\theta) - (C_{13}+C_{55})^2\cos^2\theta\sin^2\theta \qquad (\theta \text{ from Z axis}) ; \tag{11}$$

$$(k_{23}/\omega) = (2\rho)^{\frac{1}{2}}\left[C_{44}+C_{33}\cos^2\theta + C_{22}\sin^2\theta + \sqrt{(C_{44}+C_{33}\cos^2\theta + C_{22}\sin^2\theta)^2 - 4\overline{\overline{B}}}\ \right]^{\frac{-1}{2}}$$

$$\overline{\overline{B}} = (C_{44}\cos^2\theta + C_{22}\sin^2\theta)(C_{33}\cos^2\theta + C_{44}\sin^2\theta) - (C_{23}+C_{44})^2\cos^2\theta\sin^2\theta \qquad (\theta \text{ from Z axis}) \tag{12}$$

Usually PVDF is produced as a thin film. As PVDF becomes thicker, it is more difficult to pole because of the very high voltage required. The maximum thickness available is less than 1mm and the thickness of the film used in this study is 0.53mm. If the bulk wave through transmission method is used with this thin film, of the nine elastic stiffness constants, only C_{33}, C_{44} and C_{55} can be measured. To measure the other six constants, transducers need be placed on the thin side of the film, which is impossible. For those six constants, a much thicker sample is required, such as a thick plate or a cubical sample.

Ⅲ. Sample Preparation and Measurement

The test sample is a voided PVDF. For measurements, two cubical samples of PVDF are prepared by stacking thirty and thirty five films, respectively. Each PVDF sheet is aligned with the next so that the cubical samples as a whole keep the original axes orientation. The volume fraction of epoxy in the samples is kept less than 1% and the effect of epoxy on the material property of the cubical samples is considered negligible[2]. Test equipment consists of Ultran NDT transducers, a Panametrics pulse generator 5055PR, a Krohn-Hite 3202 filter and a LeCroy 9400A digital oscilloscope. The digital oscilloscope can perform FFT operations.

First, by using both the thin film and cubical samples, C^D_{33}, C^D_{44} and C^D_{55} are measured by Eqs. 6-8 over the frequency range of 150-600KHz. The results from the three samples are almost the same. There is a small difference between the results from the thin film and those from the cubical samples, but it is less than 2%. The difference is thought to be due to the addition of epoxy in the cubical samples because all the other measurement conditions are the same. To check the effect of epoxy, a cubical sample of epoxy is prepared in the same manner as the PVDF cubical samples. The epoxy sample is assumed isotropic, and in the test, only C^D_{11} and C^D_{44} are measured.

Test results show that the epoxy is a little stiffer than PVDF in both longitudinal(6.5+i0.01 GN / m²) and shear(1.7+i0.01 GN / m²) properties. Thus, the fact that the C^D_{33}, C^D_{44} and C^D_{55} of the PVDF cubical samples are slightly larger than those of the thin film is mainly due to the effect of epoxy. For the other diagonal terms C^D_{11}, C^D_{22} and C^D_{66} the thin film can not be used and measurements are made with the cubical samples only. For the non-diagonal terms C^D_{12}, C^D_{13} and C^D_{23}, obliquely incident waves have to be launched and for that purpose a plexiglass wedge is used, on which a transmitting transducer is mounted at a specific angle(45°). Measured data are presented in Table 1.

Table 1. Elastic stiffness constants of PVDF

GN / m2	measured value 150 ~ 600KHz	Ref.7 ~1KHz (real part only)
C^D_{11}	3.61+i0.10 ~ 3.69+i0.12	3.17
C^D_{22}	3.13+i0.09 ~ 3.15+i0.11	3.20
C^D_{33}	1.63+i0.12 ~ 1.64+i0.13	1.51
	(1.60+i0.12 ~ 1.61+i0.13)*	
C^D_{44}	0.55+i0.03 ~ 0.55+i0.03	–
	(0.55+i0.03 ~ 0.55+i0.03)*	
C^D_{55}	0.59+i0.02 ~ 0.59+i0.03	–
	(0.58+i0.02 ~ 0.59+i0.03)*	
C^D_{66}	0.69+i0.01 ~ 0.70+i0.02	0.7
C^D_{12}	1.61+i0.04 ~ 1.64+i0.05	1.47
C^D_{13}	1.42+i0.04 ~ 1.44+i0.05	1.23
C^D_{23}	1.31+i0.03 ~ 1.33+i0.04	1.0

( )* : measured with a thin film

The table also shows reported valuses measured at the frequency of 1 KHz[7]. Of the nine constants, data for C^D_{44} and C^D_{55} are new and no data is available to compare with. The measurements in Ref.[7] are confined to the real part of C^D_{ij} only. As seen in the table, there is some difference between the two sets of data, especially for C^D_{12}, C^D_{13} and C^D_{23}. But considering the strong frequency dependence of the properties of PVDF and the difference in the experimental methods, the comparison is fairly good.

Finally, to check the validity of the measurement technique and the accuracy of the results, the same technique is applied to a PZT-5H cubical sample(19.12mm×25.43mm×25.40mm, thickness×width×length). With the normal incidence technique, C^D_{12}, C^D_{13} and C^D_{44} are measured in the same manner as before with Eqs.4, 6 and 7. With the oblique incidence technique, C^D_{13} is measured by the Eq.13.[6].

$$(k_{13}/\omega) = (2\rho)^{\frac{1}{2}}\Big[C_{44} + C_{33}\cos^2\theta + C_{11}\sin^2\theta + \sqrt{[(C_{44} - C_{33})\cos^2\theta + (C_{11} - C_{44})\sin^2\theta]^2 + (C_{13} + C_{44})^2\sin^2 2\theta}\ \Big]^{\frac{-1}{2}} \quad (\theta \text{ from Z axis}) \qquad (13)$$

Table 2 shows the results measured at 500KHz and the known values[8]. For the known values, the imaginary parts are not available. When the real parts of our results are compared with the known values, the difference is less than 2%. Therefore, it is concluded that the measurement technique is appropriate and the results are correct within an error range of at most 2%.

Table 2. Elastic stiffness constants of PZT-5H at 500KHz

GN / m2	measured value	Ref.8
C^D_{11}	127.9	129.2
C^D_{33}	155.2	158.7
C^D_{44}	42.3	42.2
C^D_{13}	70.3	72.5

IV. Dielectric Constants

With the same samples used for the measurement of stiffness constants, complex dielectric constants are measured. For the orthorhombic mm2 symmetry, there are three independent dielectric constants. With the same axis configuration as before, they are ε_{11}, ε_{22} and ε_{33}. For the measurement, electrodes are put on the two opposite faces of the sample by using silver paint, and therefore parallel plate capacitors are made. The capacitance C and the dissipation factor D ($\tan\delta$) of the capacitors are measured with a HP 4192A LP Impedance Analyzer. They are related to the complex dielectric constants $\varepsilon=\varepsilon^r+i\varepsilon^i$ as

$$C = \varepsilon^r S / d$$
$$D = \tan\delta = \varepsilon^i / \varepsilon^r, \tag{14}$$

where S is the plate area and d is the separation between the two plates. By using this technique for all three pairs of surfaces, all three complex dielectric constants are measured at constant stress T. For ε^T_{33}, both the thin film and the cubical samples can be used. As before, the results for the two cubical samples are almost the same. But they show a difference of about 3% from those of the thin film. This difference can also be attributed to the effect of epoxy in the cubical samples. To check this, the complex dielectric constant of the epoxy sample is measured. According to the results, the dielectric constant of epoxy(4.5+i0.1) is smaller than those of PVDF. Thus, the difference is confirmed again to be due to epoxy. Measurements of ε^T_{11} and ε^T_{22} can be done only with the cubical samples of PVDF and not with the thin film samples. Measured data over the frequency range of 100-600KHz are shown in Table 3.

Table 3. Dielectric Constants of PVDF

	100KHz	~	600KHz
$\varepsilon^T_{11}/\varepsilon_0$	6.9+i0.2	+	6.3+i0.4
$\varepsilon^T_{22}/\varepsilon_0$	8.6+i0.1	+	7.9+i0.3
$\varepsilon^T_{33}/\varepsilon_0$	7.6+i0.1	+	6.8+i0.3
	(7.8+i0.1	+	7.0+i0.3)*

( )* : measured with a thin film

As before, to check the validity of using the impedance analyzer and the accuracy of the results, the same technique is applied to a PZT-5H cubical sample and the results are compared with known values[8]. Table 4 shows the results measured at 1KHz, where only the real parts of the measurement results are cmpared because the imaginary parts are not available for the known values. It also shows the dielectric constants of PVDF, for both the thin film and cubical samples measured at 1KHz and the reported value of ε^T_{33}. Comparison of our results with known values of PZT-5H shows that our results are correct within an error range of 1%. For the thin film PVDF, only ε^T_{33} could be measured, and our result is almost the same as the reported value[7]. For the cubical samples of PVDF, the measured value of ε^T_{33} differs from the reported value by 3%. ε^T_{11} and ε^T_{22} are totally new and no data is available to compare with our results. From these comparisons, it can be said that the measurement with the impedance analyzer is fairly accurate. The difference between the ε^T_{33} of PVDF cubical samples and that of the thin film is thought to be mainly due to the effect of epoxy.

Table 4. Dielectric Constants of PVDF and PZT-5H at 1KHz

	PVDF measured			PZT-5H	
	thin film	cube	Ref.7	measured	Ref.8
ε^T_{11}	—	7.35	—	3097	3130
ε^T_{22}	—	9.27	—	3097	3130
ε^T_{33}	8.05	7.75	8.0	3378	3400

V. Piezoelectric Constants

PVDF has five independent piezoelectric constants and, with the axis configuration in Fig.1, they are g_{31}, g_{32}, g_{33}, g_{15} and g_{24}. The mechanism to launch a SAW by means of IDTs on a piezoelectric medium is well known. The propagation behavior of a SAW depends on the piezoelectric material and, hence, its wave number is a function of the material properties. Based on this idea, a least square technique is used to fit optimally the piezoelectric constants to a measured SAW wave number. For measurement of the SAW wave number, a low frequency SAW device is made with a PVDF thin film, a steel substrate and silver electrodes. The size of the SAW device is 64mm×153mm×153mm(thickness×width×length). In the SAW device, there are one transmitter and two receivers separated by Δd, Fig.3. The SAW generated by the transmitter propagates to the receivers. After a delay time t_1, receiver 1 catches the signal and after a longer delay time $t_1+\Delta t$, receiver 2 does it. With the received signals and the known distance Δd between receiver 1 and 2, the phase velocity v and the attenuation coefficient α of the SAW can be calculated as in Sec.2. Then with Eq.3, an experimentally measured complex wave number k_m is determined.

Now, a least square method is used to fit this measured k_m with a numerically calculated wave number k_c obtained from modelling the low frequency SAW device. The constitutive equations of a piezoelectric material are

$$S_i = s^D_{ij} T_j + g^t_{li} D_l$$
$$E_k = -g_{kj} T_j + \beta^T_{kl} D_l \qquad (15)$$

where T is the stress, S is the strain, E is the electric field, D is the electric displacement field,

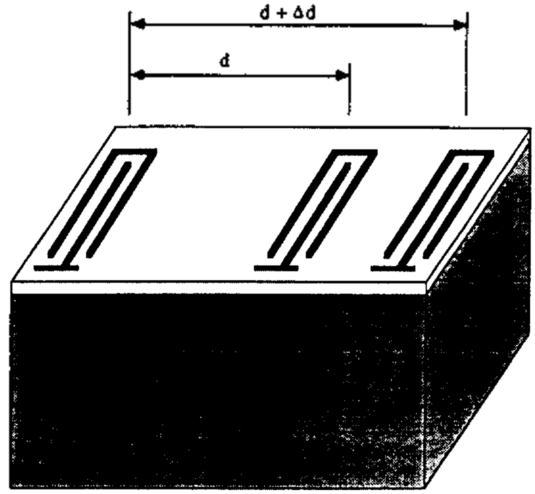

Fig. 3. Low frequency SAW device for measuring piezoelectric constants g_{ij} of PVDF

s^D is the ealstic compliance constant measured at constant D field and β^T is the impermittivity measured at constant T. $[s^D]$ is $[C^D]^{-1}$ and $[\beta^T]$ is $[\varepsilon^T]^{-1}$. C^D_{ij} and ε^T_{kl} were measured in Secs. 3& 4, and for the unknown complex piezoelectric constants g_{kl}, arbitrary values are assumed, for now. Actually, as initial guesses of the g_{kJ}, the data from Ref.[7] are used. With these complex material constants, for the center frequency ω from the measurement, a theoretical wave number k_c is claculated by a numerical simulation of a SAW propagation at the surface of the layered medium [9]. In the simulation, the influence of non-viscous air loading to the surface is taken into account. When this k_c is compared with the k_m, if the difference $[k_m - k_c]^2$ is smaller than a pre-set tolerance limit δ, the assumed values of g_{kJ} are taken as valid material constants. If the difference is bigger than δ, another assumed g_{kJ} are tried, and an iteration of the trial is continued until the $[k_m - k_c]^2$ becomes smaller than δ. In trying the new guesses of g_{kJ}, optimization algorithms are used, a direct search complex algorithm and a direct search polytope algorithm[10].

PVDF is an anisotropic material. The SAW velocity and the components of material constants involved in the SAW propagation are different for different propagation directions on the film. Careful examination of the equations of motion which the SAW should satisfy in propagation shows that when the SAW propagates in the material X axis, of the five independent piezoelectric constants, only g_{31}, g_{32}, g_{33} and g_{15} are involved in the wave propagation while in the material Y axis, g_{31}, g_{32}, g_{33} and g_{24} are involved. When the SAW propagates in between these two material axes, all the five constants are involved. In the calculation, the more unknown variables we have, the more computer time it takes and the less accurate the results are. Thus a SAW is launched in the material X axis first and g_{31}, g_{32}, g_{33} and g_{15} are calculated. Then, by launching a SAW in the material Y axis, the remaining constant g_{24} is determined. The frequency of the SAW is easily controlled by using several IDTs and the measurement is done in the frequency range of 200-600KHz. Results are shown in Table 5. Compared with C^D_{ij} and ϵ^T_{kl}, the variation of g_{kJ} with frequency is small. In the table, reported real parts of some of the piezoelectric constants are shown, too.

	measured value			Ref.7
Vm / N	200KNz	~	600KHz	1KHz
g_{31}	0.21+i0.03	~	0.21+i0.03	0.198
g_{32}	0.03+i0.01	~	0.03+i0.01	0.03
g_{33}	-0.46+i0.05	~	-0.46+i0.05	-0.48
g_{15}	-0.32+i0.02	~	-0.33+i0.02	–
g_{24}	-0.27+i0.02	~	-0.27+i0.02	–

As before, the same technique is applied to PZT-5H, of which three independent piezoelectric constants are known. Table 6 shows the results obtained at 500KHz. For the known values in the table, imaginary parts are not available. As shown in the table, measured values in general agree well with known values with maximum difference of 4%. the least square fitting of the piezoelectric constants are based on the measured values of C^D_{ij} and ϵ^T_{kl}. Hence, the results contain calculation round-off errors and experimental errors in the measurement of C^D_{ij} and ϵ^T_{kl} as well as a complex SAW wave number k_m. Considering these error factors, the comparison of the results with reported values is reasonable.

Table 6. Piezoelectric constants of PZT-5H at 500KHz

Vm / N	measured value	Ref.8
g_{31}	0.0095	-0.0091
g_{33}	-0.020	-0.019
g_{24}	0.028	0.027

Ⅵ. Conclusion

With the uniaxially oriented poled PVDF, frequency dependent all nine complex elastic stiffness constants, three dielectric constants and five piezoelectric constants were measured using both thin film and stacked, cubical samples. For the measurements, the ultrasonic technique, an impedance analyzer and the least square fitting technique were employed. To check the validity of the measurement technique and the accuracy of the results, the same techniques were applied to PZT-5H and the results showed a good agreement with known values. It is proposed that the technique used here can be generally applied to characterize the complex frequency dependent properties of a variety of piezoelectric materials with great accuracy and convenience.

References

1. G.Gerliczy and R. Betz, "New technical developments in PVDF piezoelectric devices in Europe and in the U.S.A., "Proceedings of the Sixth International Symposium on Applications of Ferroelectrics, Bethelehem, PA, June. 8-11, 1986.
2. D.Rickets, "Evaluation of the property coefficients of piezoelectric polymers", Journal of the Acoustical Society of America, Vol.85, S76, 1986.
3. Q.C.Xu, A.R. Ramachandran and R.E.Newnham, " Resonance measurement technique for complex coefficients of piezoelectric composites", Journal of Wave-Material Interaction, Vol.2, No.2, pp.105-122, April 1987.
4. E.L. Nix, "A Direct Method for Measurement of the Film-Thickness Piezoelectric Coefficient of Polyvinylidene Fluoride", Ferroelectrics, Vol.67, pp.125-130, 1986.
5. G.Kovacs, G.Trattnig, E.Langer, "Accurate determination of material constants of piezoelectric crystals from SAW veloity measurements", Ultrasonics Symposium, pp.269-272, 1988.
6. B.A.Auld, "Acoustic fields and waves in solids", Vol. 1, John Wiley & Sons, 1973.
7. R.H.Tancrell, D.T.Wilson and D.Ricketts, "Properties of PVDF polymer for sonar", Ultrasonics Symposium, pp.624-629, 1986.
8. Vernitron Piezoelectric Division "Modren piezoelectric ceramics", 1988.
9. J.J.Campbell and W.R.Jones, "Propagation of surface waves at the boundary between a piezoelectric crystal and a fluid medium", IEEE Transactions on Sonics and Ultrasonics, Vol.SU-17, No.2, pp.71-76, Apr. 1970.
10. J.A.Nedler and R.Mead, "A simplex method for function minimization", Computer Journal, Vol.7, p. 308-313, 1965.

▲**Yongrae Roh** received the B.S. and M.S. degrees in Mineral and Petroleum Engineering from the Seoul National University, Seoul, in 1984 and 1986, respectively. He got the Ph.D. degree in Engineering Science and Mechanics(major in Acoustics) from the Pennsylvania State University, U.S.A., in 1990. He is currently a senior research scientist in the Research Institute of Industrial Science and Technology, Pohang. Major research area includes SAW devices, ultrasonic transducers, and noise & vibration control. He received the 1990 Xerox Award, U.S.A., for the best research in materials.