

# Effect of Dielectric Relaxation on the Performance of P(VDF-TrFE) Copolymer Ultrasonic Transducers

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**Abstract** - The complex dielectric permittivity of vinylidene fluoride-trifluoroethylene copolymer with 20 mol% of TrFE [P(VDF-TrFE) 80/20] has been measured over the frequency range of 500 kHz to 20 MHz at temperatures varying from 20° to 100° C. This copolymer has the highest electromechanical coupling coefficient  $k_t$  among all TrFE compositions and has thus attracted considerable interest in ultrasonic transducer applications. The effect of dielectric relaxation on the performance of VDF-TrFE transducers is discussed.

## INTRODUCTION

Vinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) copolymers have been widely used in a variety of applications including pyroelectric detectors, broad-band transducers, medical ultrasound and nonlinear optics [1-2]. The dielectric relaxation in unpoled copolymers of different TrFE compositions has been extensively studied, and relaxation peaks in the high frequency range (100 kHz - 10 MHz) has been observed [3]. However, there are comparatively few reports on the dielectric relaxation behavior of poled copolymers and its effect on piezoelectric properties. As the copolymer with 20 mol% of TrFE [P(VDF-TrFE) 80/20] has the highest electromechanical coupling coefficient [4], the present work examines the dielectric relaxation in this copolymer (after poling) by determining its complex dielectric permittivity over a frequency range of 500 kHz to 20 MHz at temperatures varying from 20°C to 100°C. As the copolymer is a high-loss material, the nonlinear regression method [5], instead of the method of IEEE Std. 176-1987, is used to obtain the material parameters from the impedance data around the resonance, and then the frequency dependence of the complex dielectric permittivity is calculated.

## EXPERIMENTS

The vinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) copolymer was supplied by Atochem North America Inc. (now Amp Sensors, Valley Forge, PA). It was an extruded unpoled sheet of thickness 0.8 mm. Its Curie transition temperature for the first heating ( $T_c\uparrow$ )

and its melting temperature were 124.4°C and 149.0°C, respectively, indicating a TrFE content of slightly higher than 20% [6]. Before poling, the copolymer sheet was annealed at 120°C for two hours so as to increase the content of polar  $\beta$ -phase crystallites in the copolymer. The annealed sheet was then electroded on the surfaces with a quick drying silver paint and poled along the thickness direction. In order to enhance the piezoelectric activities of the copolymer, the sample was poled using a two-step poling process, in which the sample was poled at 105°C for two hours and then cooled down to room temperature with the electric field kept on; then the sample was repoled at 105°C for another two hours. The electric field applied to the sample was 25 MV/m. The thickness of the poled copolymer sample was then reduced to 0.355 mm (to increase the resonance frequency) and cut into a disk of diameter 10 mm. An unpoled copolymer disk was also prepared from the annealed sheet.

The impedance (both the magnitude and phase) of the copolymer disks were measured using an impedance analyzer (HP4194A). A personal computer (486DX-50) was used to collect the impedance data and to calculate the material parameters:  $k_t$ ,  $\tan\delta_k$ ,  $c_{33}^D$ ,  $\tan\delta_m$  and the frequency dependence of the complex dielectric permittivity.

## EVALUATION OF MATERIAL PARAMETERS

For a lossless resonator of thickness  $t$  and electrode area  $A$ , the electrical impedance at the thickness mode resonance is given by equation 14 in [7]:

$$Z(f) = \frac{t}{i2\pi f A \epsilon_{33}^S} \left[ 1 - k_t^2 \frac{\tan(\pi f t \sqrt{\rho / c_{33}^D})}{\pi f t \sqrt{\rho / c_{33}^D}} \right] \quad (1)$$

where  $\epsilon_{33}^S$  is the clamped dielectric permittivity,  $k_t$  is the electromechanical coupling coefficient for the thickness mode,  $c_{33}^D$  is the elastic stiffness constant at constant electric displacement,  $\rho$  is the density, and  $f$  is the frequency. To account for the losses, the material parameters  $c_{33}^D$ ,  $\epsilon_{33}^S$  and  $k_t$  are treated as complex quantities by adding an asterisk as the superscript, e.g.,

$c_{33}^{D*}$ ,  $\epsilon_{33}^{S*}$  and  $k_t^*$ , and written in the form of

$$c_{33}^{D*} = c_{33}^D (1 + i \tan \delta_m) \quad (2)$$

$$\epsilon_{33}^{S*} = \epsilon_{33}^S (1 - i \tan \delta_e) \quad (3)$$

$$k_t^* = k_t (1 + i \tan \delta_k), \quad (4)$$

where  $\tan \delta_m$ ,  $\tan \delta_e$  and  $\tan \delta_k$  are the elastic, dielectric and electromechanical coupling coefficient loss tangent, respectively. All the material parameters are assumed to be independent of frequency in the vicinity of the resonance. Substitution of equation (2) - (4) into equation (1) gives the impedance magnitude ( $|Z|$ ) and phase angle ( $\phi$ ) [5]:

$$|Z(f)| = \sqrt{R^2(f) + X^2(f)} \quad (5)$$

$$\phi(f) = \tan^{-1} \left( \frac{X(f)}{R(f)} \right). \quad (6)$$

where

$$R(f) = \frac{t \cdot \tan \delta_e}{2\pi f \epsilon_{33}^S A (1 + \tan^2 \delta_e)} + \frac{tk_t^2}{2\pi f \epsilon_{33}^S A} \frac{T - U}{S} \quad (7)$$

$$X(f) = \frac{-t}{2\pi f \epsilon_{33}^S A (1 + \tan^2 \delta_e)} + \frac{tk_t^2}{2\pi f \epsilon_{33}^S A} \frac{F + G}{S} \quad (8)$$

$$T = [\tanh N \sec^2 M (1 - \tan^2 \delta_k) - 2 \tan \delta_k \tan M \sec^2 N] \\ (M - N \tan \delta_e) \quad (9)$$

$$U = [\tan M \sec^2 N (1 - \tan^2 \delta_k) + 2 \tan \delta_k \tanh N \sec^2 M] \\ (N + M \tan \delta_e) \quad (10)$$

$$F = [\tanh N \sec^2 M (1 - \tan^2 \delta_k) - 2 \tan \delta_k \tan M \sec^2 N] \\ (N + M \tan \delta_e) \quad (11)$$

$$G = [\tan M \sec^2 N (1 - \tan^2 \delta_k) + 2 \tan \delta_k \tanh N \sec^2 M] \\ (M - N \tan \delta_e) \quad (12)$$

$$S = (M^2 + N^2)(1 + \tan^2 \delta_e)(1 + \tan^2 M \tanh^2 N) \quad (13)$$

$$M = \pi f t \sqrt{\frac{\rho}{c_{33}^D}} \left(1 - \frac{3}{8} \tan^2 \delta_m\right) \quad (14)$$

$$N = \frac{\pi f t \cdot \tan \delta_m}{2} \sqrt{\frac{\rho}{c_{33}^D}} \left(1 - \frac{5}{16} \tan^2 \delta_m\right). \quad (15)$$

Using the non-linear regression procedure (Gauss-Newton method) [5], the observed  $|Z(f)|$  and  $\phi(f)$  (200 pairs around the resonance) are fitted to (5) and (6), respectively, to obtain the six material parameters:  $c_{33}^D$ ,  $\epsilon_{33}^S$ ,  $k_t$ ,  $\tan \delta_m$ ,  $\tan \delta_e$  and  $\tan \delta_k$ .

In general, all of the six parameters depend on frequency. Therefore, each calculated material parameter represents an average within the frequency range where data points are used for the calculation. In the present work, data in the frequency range of  $3(f_n - f_m)$  centered at  $f_o$  ( $f_o = (f_n + f_m)/2$ ) are used for the calculation, where  $f_n$  and  $f_m$  are frequencies at which the impedance magnitude has a maximum and minimum, respectively.

## 1. Frequency dependence of the complex dielectric permittivity

It was shown [5] that, for PVDF and P(VDF-TrFE), the calculated impedance spectra using the measured material parameters and equations (5) and (6) agreed well with the observed spectra inside the resonance region ( $3(f_n - f_m)$  centered at  $f_o$ ). There was discrepancy between the calculated and observed values outside the resonance region. This implies that the frequency dependence of the material parameters has a significant effect on the impedance. In general, all of the six parameters depend on frequency. However, equation (1) shows that the impedance outside the resonance region is mainly contributed by the first term, therefore, as a first approximation, we calculated the frequency dependences of  $\epsilon_{33}^S$  and  $\tan \delta_e$  of the poled sample following the procedure described below.

Using an approach similar to that of Brown and Carlson [8], we inserted the values of  $c_{33}^D$ ,  $k_t$ ,  $\tan \delta_m$ , and  $\tan \delta_k$  obtained by the non-linear regression method assuming frequency-independent parameters and the observed  $|Z|$  and  $\phi$  values into (5) and (6) to calculate  $\epsilon_{33}^S$  and  $\tan \delta_e$  at each frequency [5]. Since the input values of  $c_{33}^D$ ,  $k_t$ ,  $\tan \delta_m$ , and  $\tan \delta_k$  were not exactly correct, the calculated  $\epsilon_{33}^S$  and  $\tan \delta_e$  values showed appreciable scatter in the resonance region. Therefore, we obtained smooth curves by fitting the  $\epsilon_{33}^S$  and  $\tan \delta_e$  values outside the resonance region to polynomials of order 9. Using the resulting  $\epsilon_{33}^S$  and  $\tan \delta_e$  as functions of frequency, the other four parameters were recalculated by fitting the observed impedance data in the frequency range of  $3(f_n - f_m)$  centered at  $f_o$  to (5) and (6).

For the unpoled sample, the frequency dependence of the complex permittivity ( $\epsilon$  and  $\tan \delta_e$ ) was calculated from the observed impedance data using (5) and (6), and letting  $k_t^*$  equal to zero.

## RESULTS AND DISCUSSION

The frequency dependences of the complex dielectric permittivity of the unpoled and poled copolymer samples at different temperatures are shown in Figs. 1 and 2, respectively. The material parameters of the poled copolymer calculated by the nonlinear regression method taking into account the frequency dependences of  $\epsilon_{33}^S$  and  $\tan \delta_e$  (Fig.2) are given in Table 1. The calculated impedance spectra (using equations (5) and (6)) are found to agree closely with the observed spectra. Fig. 3 shows, as an example, the good agreement between the calculated and observed impedance spectra for the poled copolymer at 40°C.

Comparing Figs.1 and 2, it can be seen that the magnitude of the dielectric permittivity and loss tangent

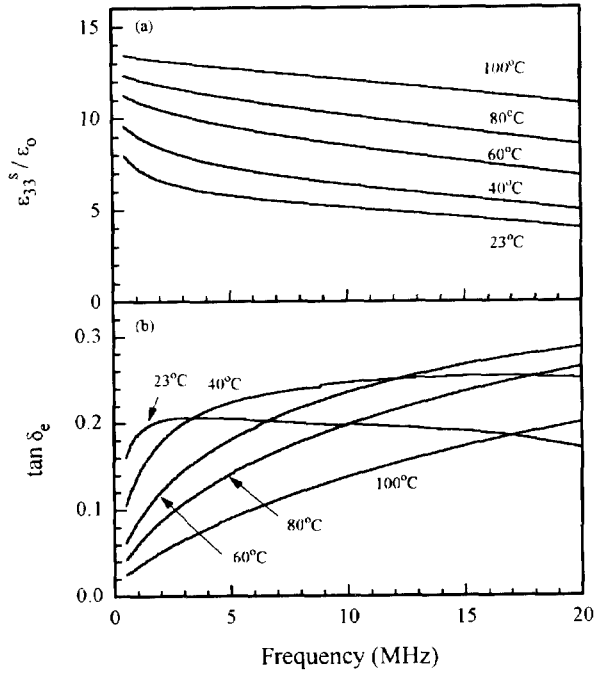


Fig.1. Variation of (a)  $\epsilon_{33}^S$  and (b)  $\tan\delta_e$  with frequency for unpoled P(VDF-TrFE) (80/20) at different temperatures.

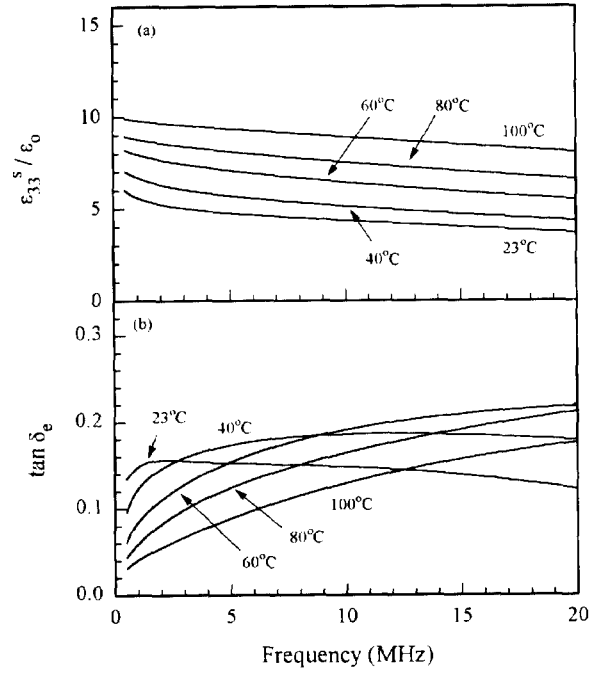


Fig.2. Variation of (a)  $\epsilon_{33}^S$  and (b)  $\tan\delta_e$  with frequency for poled P(VDF-TrFE) (80/20) at different temperatures.

of the copolymer decrease after poling, but their frequency dependences are almost unchanged. As shown in Fig. 2a,  $\epsilon_{33}^S$  of the poled copolymer at a given temperature decreases with increasing frequency. For example, the values of  $\epsilon_{33}^S/\epsilon_0$  at 23°C and 40°C decrease by about 22% as the frequency increases from 1 MHz to 10 MHz. For the poled copolymer at 23°C, a relaxation peak is observed in the frequency plot of  $\tan\delta_e$  near 2 MHz (Fig. 2b). This peak shifts to higher frequency (~12 MHz) and has a higher peak value (~0.19) as temperature increases to 40°C. As a result, the frequency dependences of  $\tan\delta_e$  are different at different temperatures in the frequency range of 1 - 10 MHz. At room temperature (23°C),  $\tan\delta_e$  decreases slightly with increasing frequency, but at higher temperature, it increases with increasing frequency and the change increases with temperature. For example, the value of  $\tan\delta_e$  at 40°C increases by about 50% as frequency increases from 1 to 10 MHz; and the increment of  $\tan\delta_e$  at 60°C is about 125%. The variation of the frequency dependence of the dielectric loss should be taken into account in designing transducers or hydrophones, as the figure of merit of the piezoelectric material is inversely proportional to the dielectric loss tangent [9].

Table 1: Material parameters of the P(VDF-TrFE) (80/20) sample at different temperatures. The  $c_{33}^D$ ,  $k_t$ ,  $\tan\delta_m$ , and  $\tan\delta_k$  values are average values within the frequency range of  $3(f_n - f_m)$  centered at  $f_0$ , while the  $\epsilon_{33}^S$  and  $\tan\delta_e$  values are those at the resonance frequency  $f_0$ .

Temperature (°C)	23	40	60	80	100
$k_t$	0.215	0.203	0.195	0.193	0.196
$\tan\delta_k$	0.049	0.058	0.036	0.029	0.024
$\epsilon_{33}^S/\epsilon_0$	5.0	6.1	7.5	8.5	9.6
$\tan\delta_e$	0.160	0.156	0.121	0.090	0.058
$c_{33}^D$ (GPa)	8.3	7.3	6.2	5.6	4.8
$\tan\delta_m$	0.089	0.088	0.077	0.071	0.067
$f_m$ (MHz)	2.83	2.65	2.47	2.33	2.17
$f_n$ (MHz)	3.06	2.86	2.64	2.49	2.31

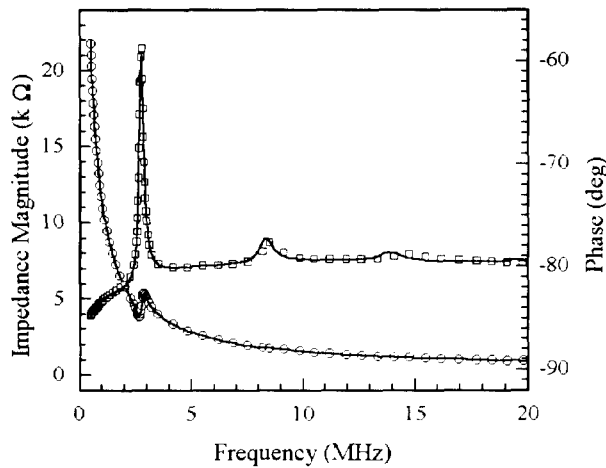


Fig.3 Comparison of calculated impedance and phase angle (solid lines) with experimental data ( $|Z|$ :  $\circ$ ; phase angle:  $\square$ ) for poled P(VDF-TrFE) (80/20) at 40°C. The material parameters used for generating the theoretical spectra are calculated by the nonlinear regression method taking into account the frequency dependence of  $\epsilon_{33}^S$  and  $\tan\delta_e$ .

As expected for a thermoplastic material, the elastic stiffness constant  $c_{33}^D$  of the poled copolymer, and hence its resonance frequencies  $f_m$  and  $f_n$  decrease with increasing temperature (Table 1). However, the electromechanical coupling coefficient  $k_t$  remains almost unchanged within the temperature range of 23° - 100°C. In order to study the thermal degradation effect on the piezoelectric properties, the poled copolymer was re-evaluated one day after it has been heated to 100°C for 10 minutes. It was found that the value of  $k_t$  decreased only by about 3%, indicating that thermal depolarization and degradation are not significant for the P(VDF-TrFE) (80/20) copolymer.

### CONCLUSION

Using the nonlinear regression method, the material parameters:  $k_t$ ,  $\tan\delta_k$ ,  $c_{33}^D$ ,  $\tan\delta_m$  and the frequency dependences of  $\epsilon_{33}^S$  and  $\tan\delta_e$  over the frequency range of 500 kHz to 20 MHz of a poled P(VDF-TrFE) 80/20 copolymer have been measured at temperature varying from 23° to 100° C. The complex dielectric permittivity of the poled P(VDF-TrFE) is lower than that of the unpoled one, but the frequency and temperature dependences are similar. The relaxation peaks of the dielectric loss tangent for both the poled and unpoled samples shifts from about 2 MHz to 12 MHz as the temperature increases from 23°C to 40 °C. The effect of thermal degradation up to 100 °C on the electromechanical coupling coefficient is not significant for the copolymer.

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