

# Dielectric Permittivity of PCLT/PVDF-TRFE Nanocomposites

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## ABSTRACT

The use of ferroelectric polymer films as pyroelectric sensors and ultrasonic transducers has attracted considerable interest. Polymer-based 0-3 nanocomposites, consisting of nanocrystalline calcium and lanthanum modified lead titanate (PCLT) powder embedded in a vinylidene fluoride-trifluoroethylene (polyvinylidenefluoride (PVDF)-trifluoroethylene (TRFE)) copolymer matrix, also have shown good potential in pyroelectric and piezoelectric applications. The dielectric permittivity and loss in these composites are important parameters characterizing their performance. In this study, the relative permittivity and loss of PCLT/PVDF-TRFE nanocomposites with various volume fractions of ceramic have been measured as function of frequency and temperature. The copolymer and nanocomposites exhibit a dielectric relaxation at the ferroelectric-to-paraelectric phase transition and another relaxation near room temperature (at  $\sim 1$  MHz). The influence of the room temperature relaxation on transducer performance is discussed.

## 1 INTRODUCTION

THE copolymers of vinylidene fluoride (VDF) and tetrafluoroethylene (TFE) have attracted considerable interest because of their use in pyroelectric sensor and ultrasonic transducer applications, see [1-3] and references therein. When the copolymer undergoes a ferroelectric to paraelectric phase transition in the crystalline regions at the Curie temperature  $T_c$ , there is a large increase in the permittivity, an abrupt change in the crystal lattice spacing and a loss of remanent polarization [4-6]. In addition to the dielectric relaxation near  $T_c$ , which is independent of the measurement frequency, there is a low temperature  $\beta$  relaxation ascribed to the local motions of short all-trans segments in the non-crystalline regions [5]. In this study, the complex permittivity of PCLT/PVDF-TRFE 0-3 nanocomposites is measured and compared to that of PVDF-TRFE.

## 2 FABRICATION OF NANOCOMPOSITES

The PVDF-TRFE 70-30 mol% copolymer supplied by Piezotech Co. has a Curie temperature of 105°C upon heating and a melting temperature of 152°C as determined by differential scanning calorimetry (see Figure 1). The procedure for preparing PCLT powder by a sol-gel method has been described in our previous report [7]. The powder used in this study was annealed at 850°C. It has an average crystallite diameter of 50 nm (determined by X-ray diffraction) and an average particle diameter of 200 nm (determined using a particle size analyzer). The

copolymer pellets were dissolved in methyl ethyl ketone (MEK), and a suitable amount of PCLT nanocrystalline powder was blended into the copolymer solution to form a mixture. The mixture was placed in an ultrasonic bath in order to disperse the powder. The mixture was then poured onto a glass plate, and a composite sheet was formed after the solvent had evaporated. The sheet was placed in an oven at 120°C for 2 h to remove the solvent completely. The dried composite sheet was cut into small pieces and then compression molded at 200°C into films  $\sim 0.2$  mm thick. By using different amounts of PCLT powder, composites with ceramic volume fraction  $\phi$  ranging from 0.15 to 0.51 were fabricated. The  $\phi$  value was calculated from the measured density  $\rho$  of the composites

$$\rho = \phi \rho_c + (1 - \phi) \rho_p \quad (1)$$

where  $\rho_c$  and  $\rho_p$  are the density of the ceramic and copolymer phases, respectively. The ceramic volume fraction calculation is based on the assumption that the volume of interface layer is much smaller than the volume of polymer matrix and their densities are almost the same. It is not possible to compare with the values expected from the amounts used because the ceramic powder that settled on the bottom after ultrasonic agitation had been discarded.

## 3 PHASE TRANSITIONS IN THE NANOCOMPOSITES

The phase transitions in the composites were studied by a differential scanning calorimeter (DSC). Composites with various  $\phi$  were subjected to a first heating from room temperature to 200°C, followed by cooling

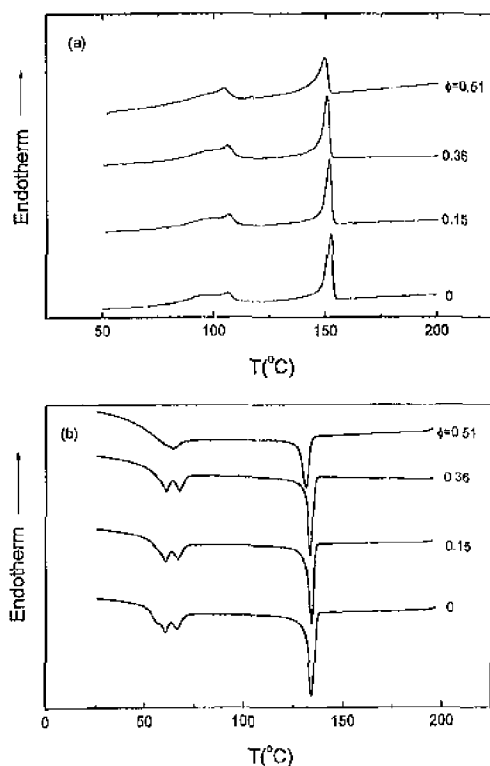


Figure 1. DSC endotherms for PCLT/PVDF-TRFE composites. (a) heating run (b) cooling run.

to room temperature at a rate of  $10^\circ/\text{min}$ . The first heating wiped out the thermal history of the samples; then a second heating and cooling cycle at  $10^\circ/\text{min}$  was carried out to obtain the endotherms. Figures 1(a) and (b) show the DSC endotherms of PCLT/PVDF-TRFE in the second heating and cooling cycle. Both the copolymer and the composites exhibit peaks in the vicinity of the Curie, melting and recrystallization temperatures of the copolymer indicating that the phase transitions of the copolymer phase are not suppressed in the composites. It is noted that the Curie transition shows thermal hysteresis:  $T_c \sim 105^\circ\text{C}$  upon heating and  $\sim 65^\circ\text{C}$  upon cooling.

A slight shift of the Curie transition peak towards lower temperatures with increasing  $\phi$  is observed in the composites. Latour *et al.* [8] suggested that defects played an important role in the Curie transition: increasing defect concentration reduced the stability of the ferroelectric phase and caused a lowering of the Curie temperature. Hence, the Curie temperature shifts observed in the composites may be ascribed to the increase in defect concentration caused by the addition of PCLT powder. Similar shift is also observed in the melting peaks, presumably also due to the same reason.

#### 4 DIELECTRIC BEHAVIOR

The complex permittivities for the PCLT/PVDF-TRFE composites were measured using a HP4194 impedance analyzer in the frequency range of 500 Hz to 10 MHz. The sample was placed in an oven whose temperature was controlled by a computer. The temperature dependency of the relative permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  at 5 kHz and 1 MHz

are shown in Figures 2 and 3, respectively. As shown in Figure 2(a),  $\epsilon'$  for all the samples upon heating increases rapidly above  $90^\circ\text{C}$  and exhibits a peak at  $\sim 105^\circ\text{C}$ , i.e. at the Curie transition temperature of the crystalline regions of the copolymer. For the copolymer and the composite at low ceramic volume fraction ( $\phi \approx 0.15$ ) the dielectric loss  $\epsilon''$  exhibits a sharp rise above  $90^\circ\text{C}$ . The dielectric loss  $\epsilon''$  arises largely from two sources, dipole relaxation and dc conduction, with the latter contribution being proportional to the dc conductivity and inversely proportional to frequency [9]. The sharp rise in  $\epsilon''$  results from the large increase in the dc conductivity of the copolymer at the Curie transition [10] and this contribution has covered up the dipolar peak. At  $\phi = 0.36$  and above, the dc conductivity contribution to  $\epsilon''$  becomes less important and a shallow peak associated with dipole relaxation can now be observed near  $100^\circ\text{C}$ . At a frequency of 5 kHz, the (relaxation associated with trans-gauche transformations of the chain segments in the non-crystalline regions of the copolymer occurs at  $\sim -20^\circ\text{C}$  [5], so only the high temperature tail of the relaxation peak is seen in our temperature range. Figure 2(b) shows the results of the cooling run at 5 kHz. The peaks in  $\epsilon'$  and  $\epsilon''$  have now shifted down to  $\sim 65^\circ\text{C}$ , again demonstrating the thermal hysteresis of the Curie transition.

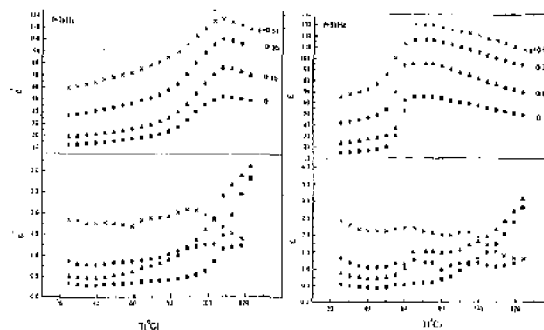


Figure 2. Relative permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  at 5 kHz of PCLT/PVDF-TRFE composites as functions of temperature. (a) heating run. (b) cooling run. Square, triangle, circle and cross denote data for  $\phi = 0, 0.15, 0.36$  and  $0.51$ , respectively.

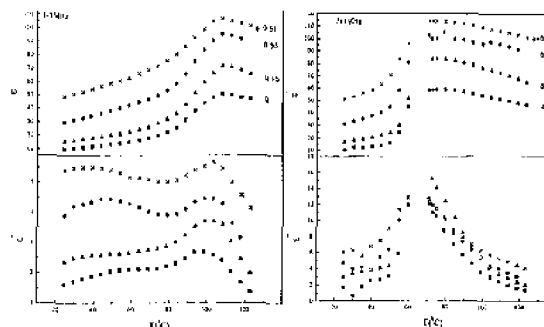


Figure 3. Relative permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  at 1 MHz of PCLT/PVDF-TRFE composites as functions of temperature. (a) heating run. (b) cooling run. Same legends as for Figure 2.

The results of the heating run at 1 MHz are shown in Figure 3(a). The temperature dependence of  $\epsilon'$  is similar to that at 5 kHz. The peak in  $\epsilon'$  also occurs at  $T_c$  ( $\sim 105^\circ\text{C}$ ), indicating that its temperature location is independent of measurement frequency. At such a high frequency the

dc conductivity contribution to  $\varepsilon''$  is not significant even at high temperatures, so the  $\varepsilon''$  relaxation peaks at  $T_c$  are clearly seen in all the samples. The relaxation has shifted to  $\sim 30^\circ\text{C}$  and is also easily observable. Comparison of the heating (Figure 3(a)) and cooling (Figure 3(b)) runs shows that thermal hysteresis of the Curie transition again occurs, and the cooling run shows a very prominent relaxation peak at  $\sim 65^\circ\text{C}$ .

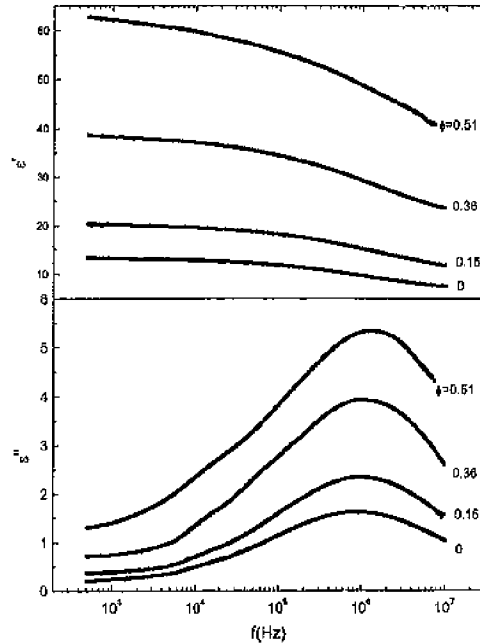


Figure 4. Relative permittivity  $\varepsilon'$  and dielectric loss  $\varepsilon''$  of PCLT/PVDF-TRFE composites at  $25^\circ\text{C}$  as functions of frequency  $f$ .

Figure 4 shows the frequency spectra of  $\varepsilon'$  and  $\varepsilon''$  at  $25^\circ\text{C}$ . The  $\beta$  relaxation peak at  $\sim 1$  MHz is conspicuous and its magnitude increases as  $\phi$  increases. Hence if the copolymer or the composite is used to fabricate transducers for room temperature operation, the dielectric loss associated with the  $\beta$ -relaxation may lower the transducer performance.

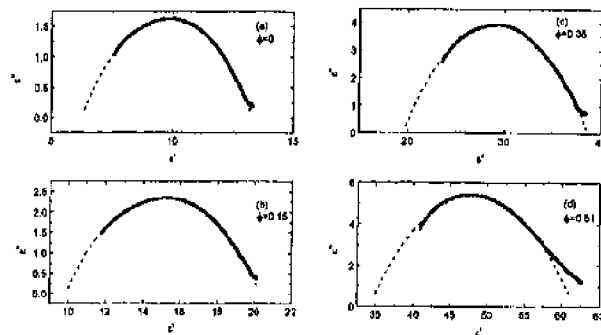


Figure 5. Cole-Cole plots for PCLT/PVDF-TRFE composites with various ceramic volume fractions  $\phi$ . The dashed lines denote the fitted curves.

In order to analyze the relaxation behavior in the composites, we choose the Cole-Cole plots [9, 11] since the relaxation in these composites is not very complicated and fits quite well to a single arc. These plots have also been used by other workers to analyze the piezoelectric relaxation in composite systems [12, 13]. The Cole-Cole plots [9, 11] at

Table 1. The values of  $\alpha$ ,  $\tau$  (in  $10^{-7}$  s),  $\varepsilon_s$  and  $\varepsilon_\infty$  for various  $\phi$  obtained from the Cole-Cole plots and Equation 2.

| $\phi$ | $\alpha$ | $\tau$ | $\varepsilon_s$ | $\varepsilon_\infty$ |
|--------|----------|--------|-----------------|----------------------|
| 0      | 0.488    | 1.80   | 13.3            | 6.28                 |
| 0.15   | 0.465    | 1.65   | 20.3            | 9.88                 |
| 0.36   | 0.507    | 1.51   | 38.7            | 19.6                 |
| 0.51   | 0.525    | 1.22   | 61.7            | 34.3                 |

$25^\circ\text{C}$  for the  $\beta$  relaxation are shown in Figure 5. The data were fitted to the following relaxation equation [9, 11]

$$\left[ \varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2} \right]^2 + \left[ \varepsilon'' + \frac{\tan(\pi\alpha/2)(\varepsilon_s - \varepsilon_\infty)}{2} \right]^2 = \left[ \frac{\sec(\pi\alpha/2)(\varepsilon_s - \varepsilon_\infty)}{2} \right]^2 \quad (2)$$

The permittivity at infinite frequency  $\varepsilon_\infty$ , the permittivity at zero frequency  $\varepsilon_s$  and the parameter  $\alpha$  are obtained from fitting the experimental data to Equation (2). The relaxation time  $\tau$  is found from the peak frequency  $f_m$  of the  $\varepsilon''$  vs. frequency plot

$$\tau = \frac{1}{2\pi f_m} \quad (3)$$

From Table 1, it can be seen that  $\alpha$  increases slightly with increasing  $\phi$ , implying that the distribution of the relaxation time broadens after PCLT powder is added. This is probably due to the effect of the ceramic/polymer interface. The relaxation time  $\tau$  decreases slightly with increasing  $\phi$  indicating that the relaxation process is facilitated by the presence of the ceramic powder. The much higher  $\varepsilon'$  and  $\varepsilon''$  for a composite as compared to those of the polymer arise from the presence of ceramic particles. The ceramic particles also lead to higher  $\varepsilon_s$ ,  $\varepsilon_\infty$  and  $(\varepsilon_s - \varepsilon_\infty)$  values. Therefore the increase of  $(\varepsilon_s - \varepsilon_\infty)$  from 7 to 27 when  $\phi$  increases from 0 to 0.51, merely reflects the increase in the ceramic particle content.

## 5 CONCLUSION

IN this work, the complex dielectric permittivity of PCLT/PVDF-TRFE 0 to 3 nanocomposites has been studied. Similar to the copolymer, there are two dielectric relaxations in the composites. The first relaxation is associated with the Curie transition in the crystalline regions and its temperature location is independent of measurement frequency (Figures 2 and 3). The second relaxation ( $\beta$ ) is ascribed to the local motions of short chain segments in the non-crystalline regions and the temperature at which it occurs increases with increasing frequency. At lower frequency, e.g. 5 kHz, the  $\beta$  relaxation peak for the 70/30 PVDF-TRFE copolymer is located at  $\sim -20^\circ\text{C}$  [5]. The  $\beta$  relaxation shifts to higher temperature with increasing frequency and occurs near room temperature at a few MHz (Figure 4). Therefore, if we use the copolymer or the composite to fabricate ultrasonic transducers operating in the MHz region, the dielectric loss may affect the performance of the transducer.

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