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Dielectric behaviour of thin films of β-PVDF/PZT and β-PVDF/BaTiO$_3$ composites

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Thin films of the composites formed between poly(vinylidene fluoride) (PVDF) and lead zirconium titanate (PZT) and also barium titanate with 0–3 connectivity, have been obtained by dispersion of the ceramic powder in a solution of PVDF in dimethylacetamide DMA. Evaporation of the solvent at 65 °C allowed crystallization of PVDF predominantly in the polar β phase, regardless of the amount of PZT or BaTiO$_3$ powder added upto 40 vol %. The relative permittivity and loss index values were determined for the pure components and for the composites with different ceramic contents, in the frequency range of 100 Hz to 13 MHz. An increase in PZT or BaTiO$_3$ content resulted in an increase in the relative permittivity of the composites, and the experimental results are shown to be in good agreement with those calculated from the theoretical expression of Yamada *et al.* [1]. The dc electrical conductivity of composites with different compositions was also determined.

1. Introduction

Ferroelectric ceramics, such as lead zirconium titanate (PZT) and barium titanate (BaTiO$_3$), with very high pyro and piezoelectric constants, are used in a variety of applications. However, the fragility, inflexibility and poor processibility, inherent to ceramics, can limit these applications. Ferroelectric polymers, such as poly (vinylidene fluoride) (PVDF) and its copolymers have been mainly used in transducers, since they are flexible, easy to process and present low mechanical impedance. However, the low pyro and piezoelectric constants of these materials together with the difficulty of polarizing thick films also restricts their application. Heterostructural materials, such as polymer–ceramic composites, have received a lot of attention recently, since these materials can combine the excellent pyro and piezoelectric properties of ceramics with the flexibility, processing facility, levity and strength of polymers. Amongst the most widely studied composites are those consisting of PVDF or its copolymers and PZT or BaTiO$_3$ [1–11]. The most simple are those that present 0–3 connectivity [12], that is usually formed by a three-dimensionally bound polymer matrix containing ceramic particles. Such composites are of interest because of their versatility towards taking on a variety of shapes, including very flexible thin films.

The most common preparation techniques for these composites are (a) hot compression of a mixture of ceramic powder and polymer powder or melt, and (b) dispersion of the ceramic powder in a solution of polymer in a convenient solvent, followed by its deposition on a substrate and finally evaporation of the solvent by heating. When the polymer used is PVDF, the former technique usually leads to the apolar α phase. The latter technique may result predominantly in either the α or β phase, or in a mixture of these, depending on the temperature at which the evaporation of the solvent took place [13]. Temperatures lower than 70 °C result predominantly in the polar β phase.

The aim of the current work was to study the dielectric properties of thin films of PVDF/PZT and PVDF/BaTiO$_3$ composites with 0–3 connectivity at different ceramic contents with PVDF in the polar β phase.

2. Experimental procedure

Composites of PVDF with PZT [$(PbZr_{0.53}Ti_{0.47})O_3$] and with BaTiO$_3$ were prepared by dispersing the ceramic powder in a solution of PVDF in dimethylacetamide (DMA). The initial concentration of the solution was 0.2 g PVDF (Foraflon® F4000–Atochem) per ml DMA. The average PZT and BaTiO$_3$ particle diameter was 1.5 and 0.6 μm, respectively. Highly flexible 18 μm films were obtained by spreading the suspension on a glass plate which was then maintained at 65 °C for 1 h, this is sufficient time for evaporation of the solvent. A temperature of 65 °C was chosen in order to allow crystallization of the β phase of PVDF [13]. Next, the samples were heated in an oven at 80 °C for 12 h in order to remove any remaining traces of the solvent. The volume percentage of the ceramic varied from 10–40%. Percentages higher than 40% were not used in order to guarantee 0–3 connectivity and to maintain the high flexibility of the films. In order to enable measurement of the dielectric properties of pure PZT and $BaTiO_3$ 1 mm thick pellets of these materials were obtained by isostatic compression of the powder followed by sintering at 1200 °C for 3.5 h

The determination of the crystalline phase of the PVDF present in each sample was achieved by IR spectroscopy (Perkin Elmer, model 283) in the range between 400–1000 cm^{-1}. The spectra of the films of pure PVDF and of the composites were obtained directly from the samples used for the electrical measurements. The spectra of the PZT and $BaTiO_3$ powders were obtained from 150 μm thick KBr pellets.

The relative permittivity (ε') and the loss index (ε'') were calculated from the capacitance and the phase angle, measured by means of an LF impedance analyser (HP–4192A) in the range of 100 Hz to 13 MHz. The dc electrical conductivity (σ) of the composites was determined from the conduction current (I_c) by using an electrometer (Keithley–610C) and a high voltage supply (Keithley–247). The I_c value was obtained after a 4 h application of a 3×10^4 V cm^{-1} electric field. This time of application was sufficient for cessation of the transient current (absorption current). Circular aluminium electrodes of 2 cm^2 area were vacuum evaporated on both sides of each sample. All measurements were carried out at room conditions (T = 25 °C and rh = 80%).

3. Results and discussion

Fig. 1 shows the IR spectra of PVDF, PZT and of two PVDF/PZT composites with different compositions. The spectra of $BaTiO_3$ and of three PVDF/$BaTiO_3$ composites are presented in Fig. 2. As expected the PVDF spectrum shows absorption bands at 511 and 840 cm^{-1} (indicated in the figures), that are characteristic of the β phase. The 490 and 880 cm^{-1} bands also present in the figures are common to the α, β and γ phases and therefore cannot be used to uniquely characterize a phase. PZT and $BaTiO_3$ strongly absorb at wave numbers under 700 cm^{-1}, making identification of the 511 cm^{-1} band difficult for composites with ceramic contents over 20 vol %. However, in the range between 700 and 1000 cm^{-1} one can note the permanence of the 840 cm^{-1} band and the absence of bands characteristic of the α phase (766, 795, 855 and 976 cm^{-1}) and the γ phase (778, 812, and 834 cm^{-1}). This result, observed for all the composites studied, shows that during crystallization of PVDF from solution, addition of the ceramic powder at the volume percentages studied, does not alter the nature of the resulting crystalline phase. For all composites the PVDF remained predominantly in the β phase. Previous workers have shown, using the IR spectroscopic technique that the presence of $BaTiO_3$ [2] or of PZT [3] introduces variations in the PVDF morphology. Disagreement between these results and ours →

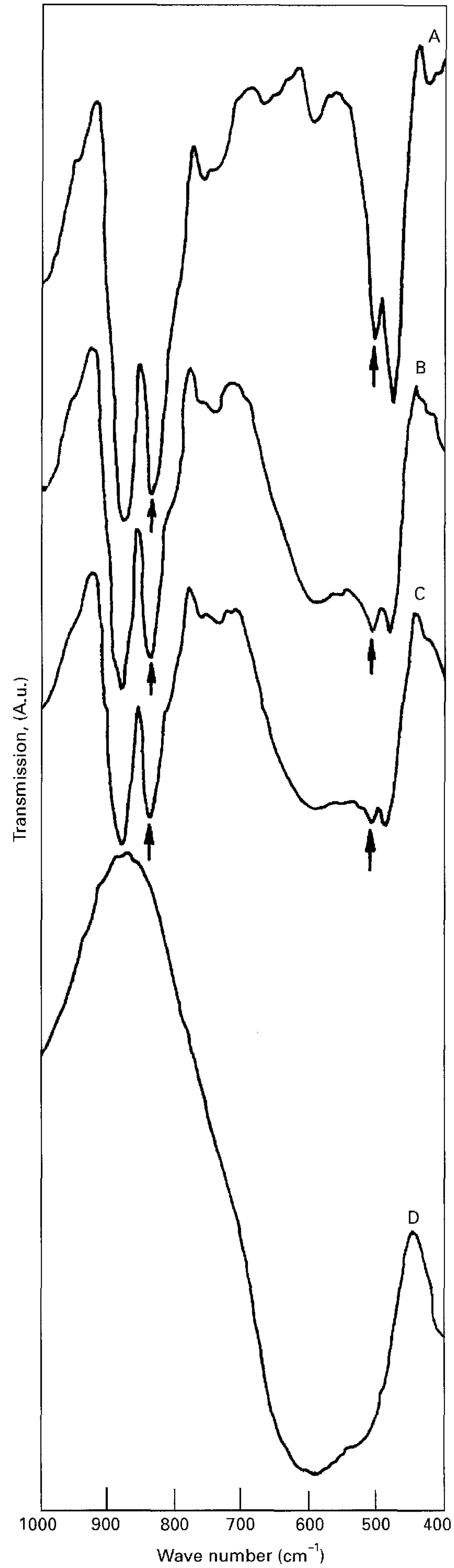

Figure 1 IR spectra of PVDF (A), of the composites PVDF/PZT of composition 90/10 (B) and 80/20 (C) and of PZT (D). Arrows indicate the 511 and 840 cm^{-1} absorption bands characteristic of the PVDF β phase.

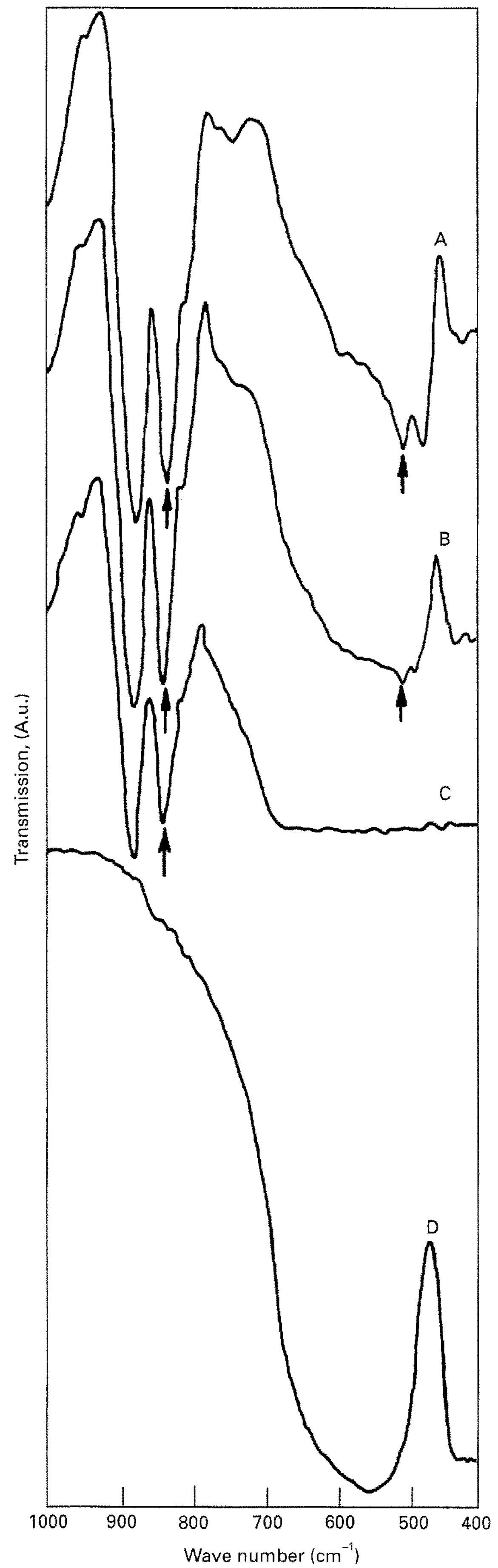

Figure 2 IR spectra of the composites PVDF/BaTiO$_3$ of composition 90/10 (A), 80/20 (B), 70/30 (C) and of BaTiO$_3$ (D).

may be related to the type of sample used for obtaining the IR spectra. Muralidhar *et al.* [2] used KBr pellets containing pure PVDF powder and also mixtures of PVDF and BaTiO$_3$ with different compositions. In our case the spectra were obtained from the same PVDF films and composites used in the electrical measurements. We only used KBr pellets for the spectra of the PZT and BaTiO$_3$ powders.

Figs (3–5) present the variations of ε′ and ε″ with the logarithm of frequency for the PVDF, PZT

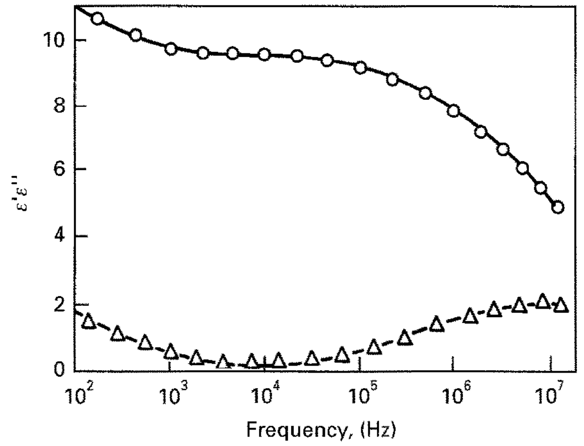

Figure 3 Variation of, (○) ε′ and, (△) ε″ with log*f* for the β PVDF sample.

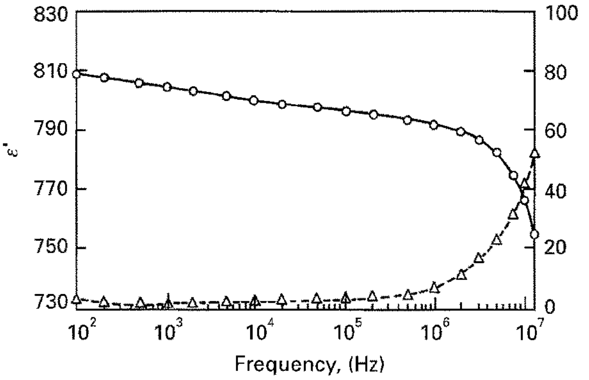

Figure 4 Variation of, (○) ε′ and, (△) ε″ with log*f* for the PZT sample.

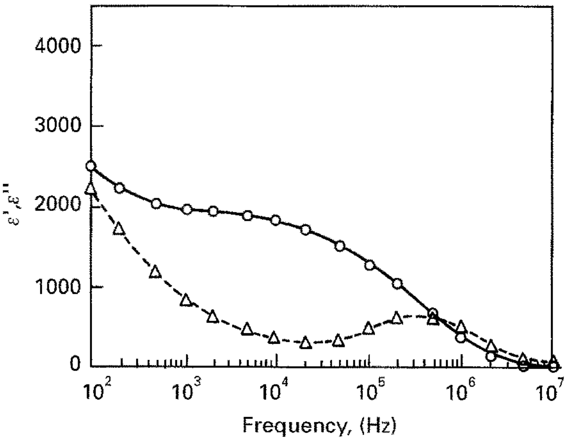

Figure 5 Variation of, (○) ε′ and, (△) ε″ with log*f* for the BaTiO$_3$ sample.

and BaTiO$_3$ samples, respectively. For PVDF one can note a maximum for ε'' near 9 MHz (absorption frequency), attributed to the orientation of the existing dipole moments in the material. At room temperature this maximum was observed for PVDF samples in the α and β phase, whether or not oriented [14]. For PZT the frequency at which ε'' peaked is greater than 13 MHz, therefore being out of the range of our measurements. The increase in ε'' observed at high frequencies probably has as its main cause the losses that take place because of the movement of domain walls in the dipolar polarization process. BaTiO$_3$ exhibits a maximum of ε'' close to 0.4 MHz, which is also attributed to losses due to domain wall movements. All three materials show an increase in ε' and ε'' towards low frequencies. This effect, which is relatively small for PZT and very intense for BaTiO$_3$ is probably related to the d.c. conductivity as well as to interfacial polarization caused by inhomogeneity in the materials. For PVDF this effect was practically suppressed when the measurements were carried out in a dry environment [14].

Figs 6 and 7 show, respectively, the variations of ε' and ε'' with log*f* for the PVDF/PZT composites with different PZT volume percentages. Figs 8 and 9 present these same variations for the PVDF/BaTiO$_3$ composites. For both composites ε' increased with the volume percentage of the ceramic, with the sole exception of the 60/40 PVDF/BaTiO$_3$ composite at $f > 0.5$ MHz, where the ε' values were inferior to those of the 80/20 and 70/30 composites. Table I presents the values of ε' at 1 kHz for the two composites with different compositions.

The variation of ε' with volume percentage of ceramic is presented in Fig. 10 for the two composites. In this figure we also presented the theoretical curves obtained from the expression developed by Yamada *et al.* [1], which relates the ε' value of the composite with the ε' values of the components:

$$\varepsilon' = \varepsilon'_p\left[1 + \frac{nq(\varepsilon'_c - \varepsilon'_p)}{n\varepsilon'_p + (\varepsilon'_c - \varepsilon'_p)(1 - q)}\right] \qquad (1)$$

where ε'_p and ε'_c are the relative permittivity of the polymer matrix and the ceramic particles, respectively, q is the volume fraction of these particles and n a parameter related to the geometry of these particles, in this case considered ellipsoidal. The ε'_p values of PVDF and the ε'_c values of PZT and BaTiO$_3$ obtained from

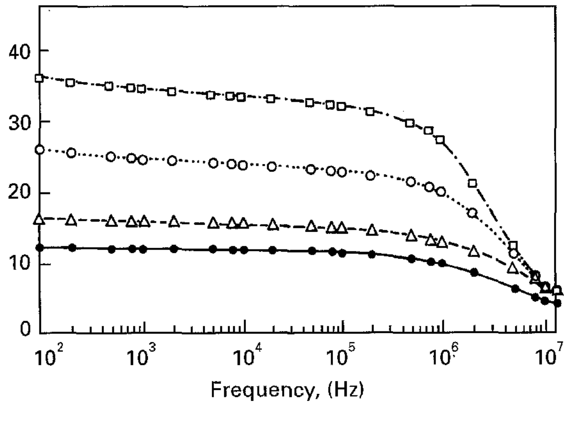

Figure 6 Variation of ε' with log*f* for the PVDF/PZT composites with different volume percentage of PZT. The PVDF/PZT compositions being, (●) 90/10, (△) 80/20, (○) 70/30 and (□) 60/40.

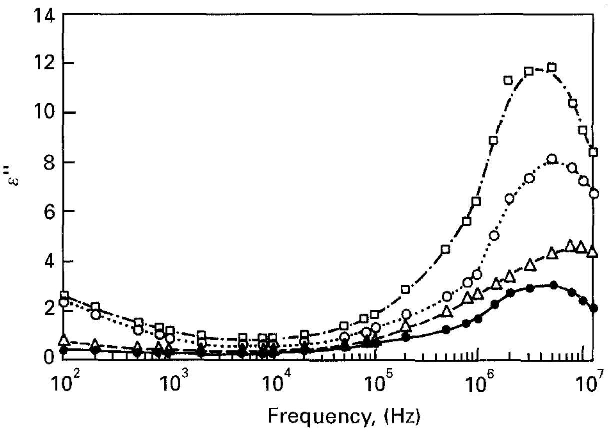

Figure 7 Variation of ε'' with log*f* for the PVDF/PZT composites with different volume percentage of PZT. The compositions being, (●) 90/10, (△) 80/20, (○) 70/30 and (□) 60/40.

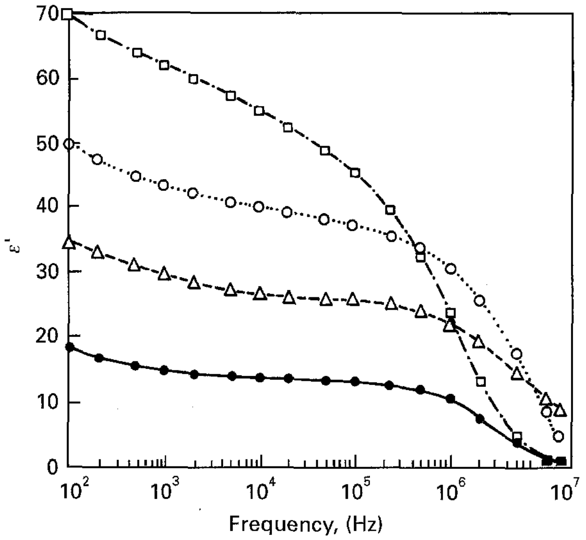

Figure 8 Variation of ε' with log*f* for the PVDF/BaTiO$_3$ composites with different volume percentage of BaTiO$_3$. The compositions being, (●) 90/10, (△) 80/20, (○) 70/30 and (□) 60/40.

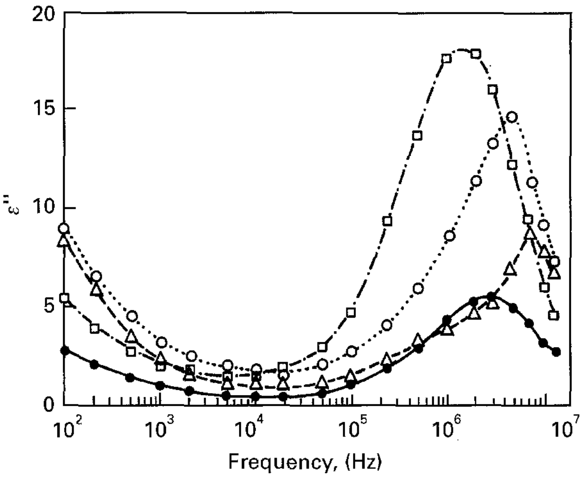

Figure 9 Variation of ε'' with log*f* for the PVDF/BaTiO$_3$ composites with different volume percentage of BaTiO$_3$. The compositions being, (●) 90/10, (△) 80/20, (○) 70/30 and (□) 60/40.

TABLE I Relative permittivity for $f = 1$ kHz and d.c. conductivity for the composites with different compositions

vol % ceramic	PVDF/PZT		PVDF/BaTiO$_3$	
	ε'	$\sigma \times 10^{-12}$ (S cm^{-1})	ε'	$\sigma \times 10^{-12}$ (S cm^{-1})
10	12.1	1.0	15.1	2.6
20	15.8	1.3	29.7	3.4
30	24.8	1.5	43.5	4.7
40	34.5	1.8	63.5	6.7

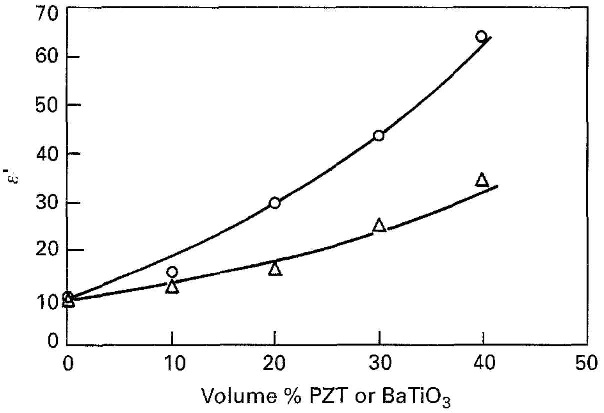

Figure 10 Variation of ε' ($f = 1$ kHz) with the volume percentage of the ceramic material for the two composites. The continuous lines were obtained from Equation 1, with $n = 8.5$ for the, (O) PVDF/BaTiO$_3$ composites and with $n = 3.5$ for (△) PVDF/PZT.

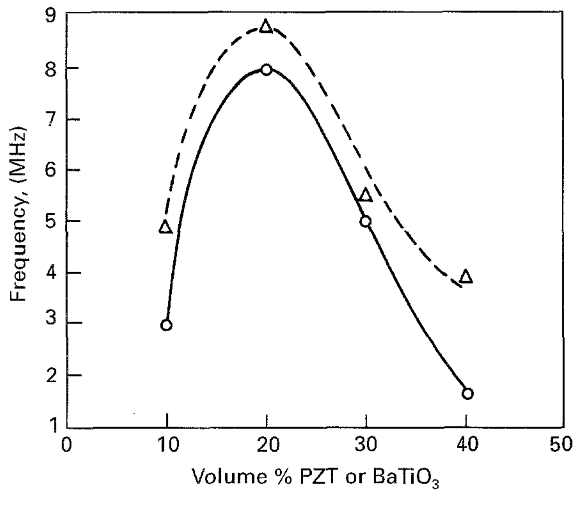

Figure 11 Absorption frequency of the dipolar polarization as a function of the volume percentage of ceramic material for the two composites. The composites being represented by (△) PVDF/PZT and (O) PVDF/BaTiO$_3$.

Figs 3, 4 and 5, respectively, were 9.8, 805 and 2000. The values of n which best fit the theoretical values calculated from Equation 1, with those obtained experimentally were 3.5 and 8.5, respectively, for the composites with PZT and BaTiO$_3$. The difference between the n values of the two composites is probably related to the different geometries of the particles, of which the average diameters were quite distinct (0.6 μm for BaTiO$_3$ and 1.5 μm for PZT).

From Figs 7 and 9 one observes that ε'' presents a maximum in the high frequency range for the two composites which is attributed to the losses caused by movement of domain walls in the ceramic materials and also to orientation of the dipole moments in PVDF. The frequency at which this maximum occurs shifts in a similar manner according to the volume percentage of the ceramic for both composites. At percentages below 20% the f value shifts to higher values. Above 20% this shift inverts. The cause of this behaviour, which can be better observed in Fig. 11, is still unknown.

The PVDF/BaTiO$_3$ composites show an increase in ε' and ε'' with a decrease in frequency for $f < 10$ kHz. This behaviour, similar to that observed for pure BaTiO$_3$ becomes more intense with increasing volume percentage of this material (with the exception of ε'' for the 60/40 composition), indicating its strong influence on the interfacial polarization and dc conduction process.

Table I also shows the σ values for the composites with different compositions. Both composites show an increase in σ with the ceramic content. It can further be noted that the BaTiO$_3$ composites present σ values superior to those of PZT, and this might be the main cause of the strong increase in ε'' observed at low frequencies.

4. Conclusions

In the crystallization of PVDF from a DMA solution, the addition of up to 40 vol % BaTiO$_3$ or PZT powder does not alter the resulting crystalline phase. Thin and highly flexible films of PVDF/PZT and PVDF/BaTiO$_3$ composites with PVDF predominantly in the polar β phase can be manufactured by deposition of the PVDF solution in DMA, in which the ceramic powder has been dispersed, on a glass substrate followed by evaporation of the solvent at T < 70 °C.

The ε' values of these composites increase with the ceramic content in agreement with the theoretical expression developed by Yamada *et al.* [1]. This increase is more pronounced for the composites in which the ceramic material presents higher ε' values. Both composites presented high ε'' values in the high frequency range, probably due to the losses caused by movements of domain walls and also dipolar orientation. The composites containing BaTiO$_3$ presented high ε'' values at low frequencies (< 1 kHz), the most probable cause being interfacial polarization, caused by the nonuniformity of the conductivity, and the dc conduction, the latter being much higher than that presented by the PZT composites.

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