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Dielectric behaviour of barium titanate–polyvinylidene fluoride composites

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The dielectric behaviour of composites of barium titanate ($BaTiO_3$) and polyvinylidene fluoride (PVDF) has been studied by changing the weight fraction of $BaTiO_3$. The dielectric behaviour of the composites has a significant influence of PVDF up to 50 wt% $BaTiO_3$ in the composite, but this effect is insignificant at higher weight fractions of $BaTiO_3$. X-ray diffraction studies on composites are also reported to correlate the observed dielectric changes with the corresponding structural changes.

1. Introduction

In recent years polymer–ceramic composites have assumed significance because of their improved properties. However, almost no work has been reported on the dielectric behaviour of any polymer–ceramic composite system by changing the volume or weight fractions of the constituents at different frequencies and temperatures to reveal the nature of the composite. Therefore in the present work it has been found desirable to make a detailed study of the same on composites of barium titanate ($BaTiO_3$) and polyvinylidene fluoride (PVDF) by changing the weight fraction of $BaTiO_3$ in the system.

In our previous work [1] we have reported how the dielectric behaviour of $BaTiO_3$–PVDF composites changes by changing the weight fraction of $BaTiO_3$; also the dielectric behaviour of $BaTiO_3$–PVDF composites of 70 wt % $BaTiO_3$, which have a high dielectric constant among other compositions, has been studied in detail at different temperatures and frequencies [2]. Cherqaoui *et al.* [3] and Takeuchi *et al.* [4] have studied the dielectric behaviour of $BaTiO_3$–PVDF composites by changing the volume fraction of $BaTiO_3$.

2. Experimental procedure

The preparation of the composite films by a solvent-cast technique has been given in detail in our paper [1]. The dielectric measurements were done with an HP 4192A LF impedance analyser.

3. Results and discussion

Figs 1 to 4 show the temperature dependence of ε' and $\tan\delta$ of $BaTiO_3$–PVDF composites of 10, 30, 50 and 70 wt % $BaTiO_3$ at various frequencies. Fig. 5 shows the temperature dependence of ε' and $\tan\delta$ of PVDF at various frequencies. The rise in ε' at 1 kHz seems to be mainly due to the inhomogeneous conduction which arises from interfacial polarization between PVDF and $BaTiO_3$ in addition to the domain contribution in the composites (Figs 1 and 3). This can be further supported by the high values of $\tan\delta$ at 1 kHz in the composites (Figs 2 and 4). ε' and $\tan\delta$ increase in the composites as the temperature increases at 1 kHz because the inhomogeneous conduction increases. In our previous paper [2] we have already proved in 70 wt % $BaTiO_3$ composites that at low frequencies below 1 kHz the losses are mainly from conduction losses rather than ferroelectric losses, as the area under the hysteresis loop is small with smaller values of P_{Sat} (saturation polarization) and P_r (remanent polarization); from 10 kHz to 1 MHz the contribution is from domains, and at 10 MHz the contribution is from domain walls. It can be seen from Fig. 2 that the peak at 10 MHz for the composites of 10, 30 and 50 wt % $BaTiO_3$ corresponds to the relaxation peak of PVDF. The loss at 10 MHz in 70 wt % $BaTiO_3$ composite is attributed to domain wall motion whose natural frequency coincides with the frequency of the applied field, which in effect gives rise to dielectric dispersion near the gigahertz region [2] (Fig. 4). Unlike the relaxation frequency, the resonance frequency shows high stability and weak dependence on temperature and other influences, as can be seen in Fig. 4, where the dependence of $\tan\delta$ on temperature is not much at 10 MHz. It is clear from the above figures and from the above explanations that PVDF seems to have a significant influence on $BaTiO_3$–PVDF composites, especially at lower weight fractions of $BaTiO_3$ (i.e. up to 50%), and this influence has been drastically reduced for composites of higher weight fractions particularly above 70% onwards. The studies have not been done on 90 wt % $BaTiO_3$ composities because of the poor connectivity, which will be reflected very much in properties like a low pyroelectric coefficient and a low dielectric constant [1]. A similar type of conduction loss, dominating the ferroelectric losses, has been observed in Fe_2O_3 and ZnO-doped $BaTiO_3$ by Thomann and Heydrich [5]. ε'' increases significantly at low frequencies and is attributed to ionic conduction by Das Gupta and Doughty [6] in composites of polypropylene (PP) and PZT (Lead Zirconate Titanate). Also the increase in ε'' with decreasing frequency is attributed to d.c. conductivity in the epoxy phase of epoxy–PZT composite by Furukawa and Fukada [7]. The d.c. conduction of

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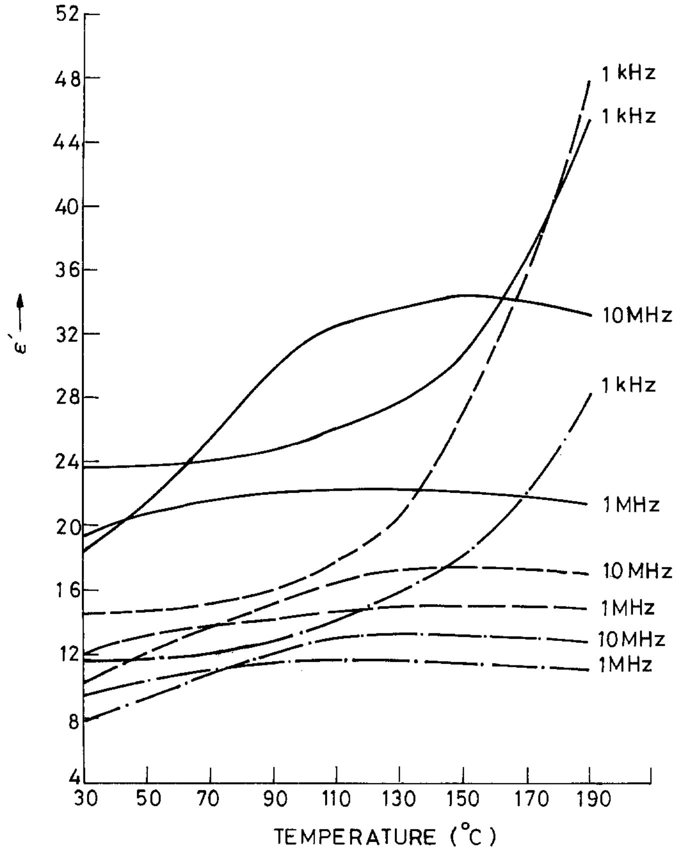

Figure 1 Temperature dependence of ε' for $BaTiO_3$–PVDF composites of (–·–) 10, (– – –) 30 and (——) 50 wt% $BaTiO_3$.

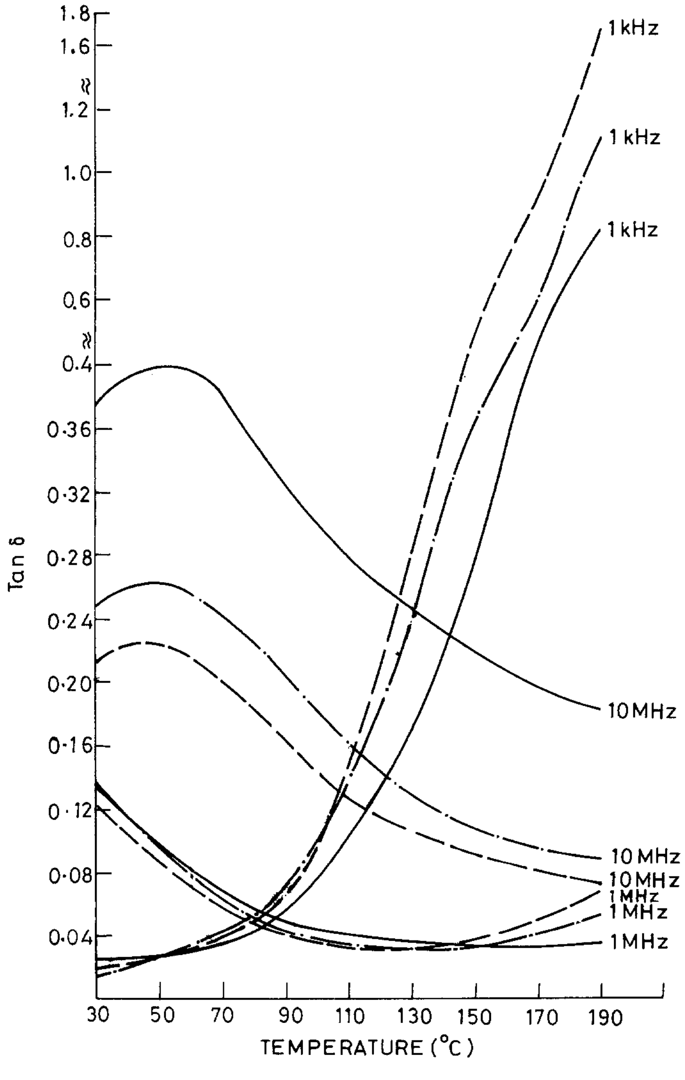

Figure 2 Temperature dependence of tanδ for $BaTiO_3$–PVDF composites of (–·–) 10, (– – –) 30 and (——) 50 wt% $BaTiO_3$.

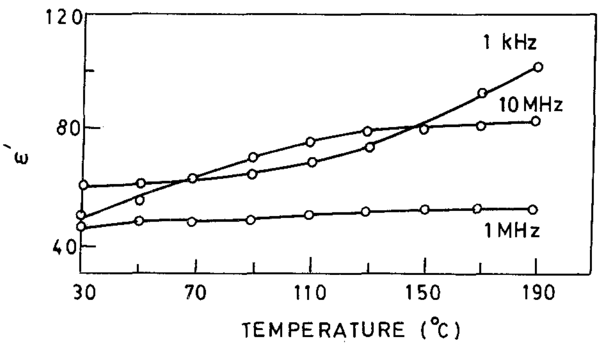

Figure 3 Temperature dependence of ε' for $BaTiO_3$–PVDF composite of 70 wt % $BaTiO_3$.

ionic impurities forms space-charge layers at the interface of inclusions and matrix in a composite [7]. Furukawa *et al.* [8] have explained the monotonous increase of ε'' with decreasing frequency on the basis of the conductivity due to ionic impurities which is considerably high between 80 and 130° C in composites of polyvinylacetate (PVA) and PZT. The first increase of ε' observed at 80° C will be ascribed to the accumulation of ionic impurities at the interface between PVA and PZT. The second increase of ε' at higher temperatures will be ascribed to the electrode polarization. Das Gupta [9] has observed that the dielectric constant values of PP–$BaTiO_3$ composites are almost unaffected by frequency, and the dissipation factor has a surprisingly low value over the whole frequency

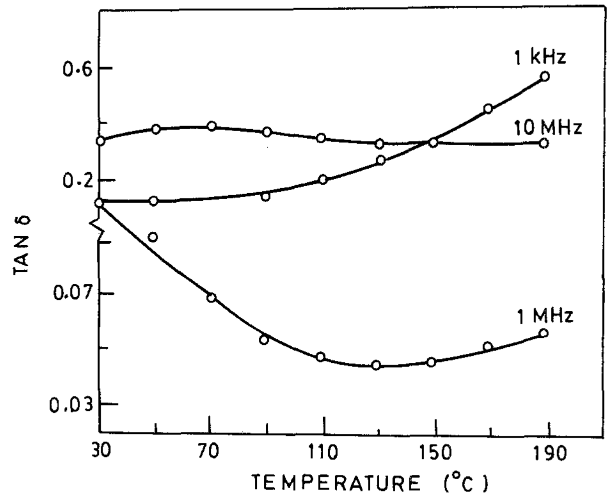

Figure 4 Temperature dependence of tanδ for $BaTiO_3$–PVDF composite of 70 wt % $BaTiO_3$.

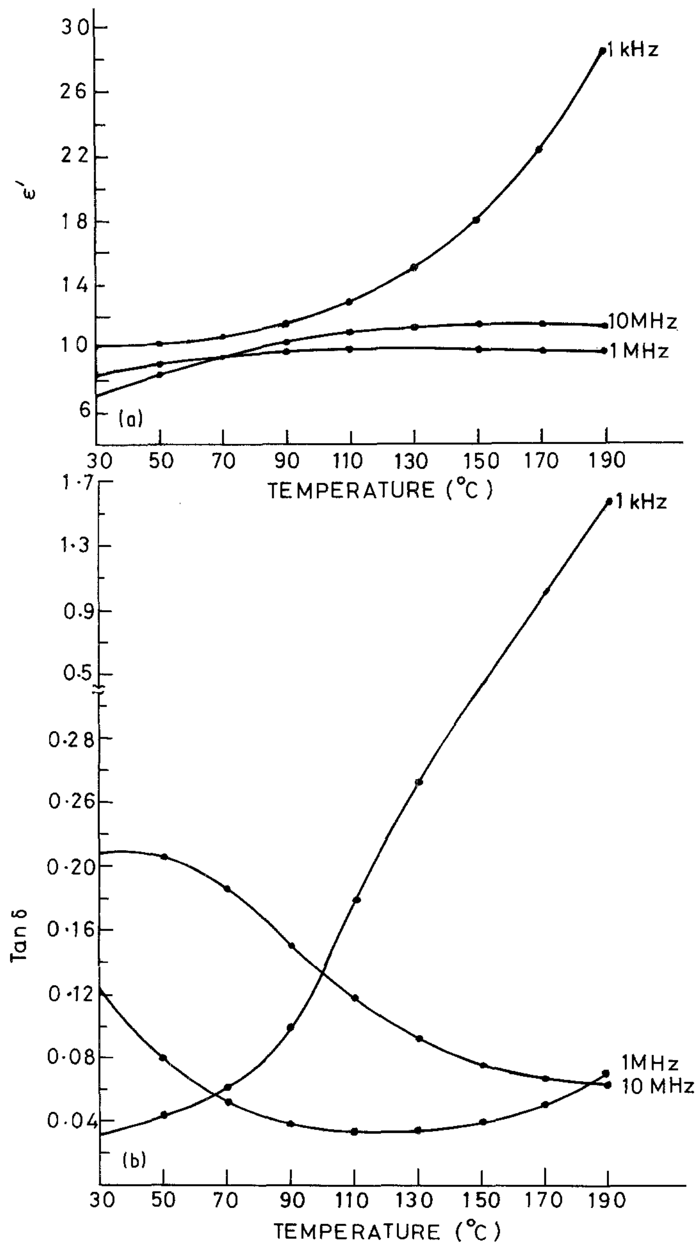

Figure 5 Temperature dependence of (a) ε' and (b) tanδ for PVDF.

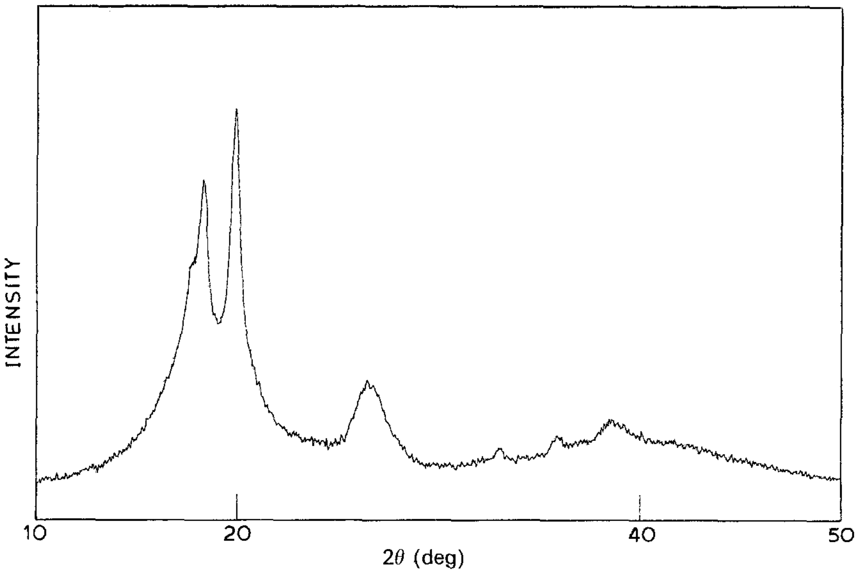

Figure 6 XRD pattern of PVDF.

range. Also samples subjected to d.c. fields of 2 to 10 kV across a 0.5 in. (12.7 mm) separation showed no significant change in dielectric constant.

Sa-Gong *et al.* [10] controlled the conductivity of the composite by adding small amounts of a semiconductor filler such as carbon, germanium or silicon. The carbon particles were trapped between PZT grains and created continuous electric flux paths between the PZT particles, leading to full poling of the composite. They got very much enhanced results of the product of piezoelectric voltage coefficient (g_h) and strain coefficients (d_h) and observed that when the amount of carbon in the composite exceeds 1.5 vol %, the loss tangent rises dramatically making it difficult to apply the large voltages required for poling. The values of $\tan\delta$ of the composites containing a conductive phase are about twice that of a composite prepared without a semiconductive phase.

We felt from the work of Sa-Gong *et al.* [10] that the conduction current is increasing by adding semiconductor filler to the composite, and the increase in $\tan\delta$ values with and without filler to the composite justified our assumption. Also we believed that if the volume percentage of the semiconductor filler increases beyond a certain level in the composite, then the conduction current increases rapidly which in turn increases $\tan\delta$ very significantly, thereby making the composite difficult to pole. This assumption is also justified by their observation that when the amount of carbon in the composite exceeds 1.5 vol %, the loss tangent rises dramatically making it difficult to apply the large voltages required for poling. The enhancement of $g_h \cdot d_h$ seems to be mainly from the conduction current. Generally compositions which are highly conductive are difficult to pole, tend to overheat and have considerable dielectric loss, which thus limits their efficiency.

Some of the peaks due to PVDF in the X-ray diffraction spectra (XRD) have been significantly reduced and some are absent from 70 wt % $BaTiO_3$ composites onwards, as explained in detail elsewhere [11]. The results are explained on the basis of internal stresses which vary from composition to composition as the interaction between PVDF and $BaTiO_3$ varies. Figs 6 to 9 show the X-ray diffraction (XRD) patterns of PVDF, $BaTiO_3$–PVDF composites of 50 and 70 wt % $BaTiO_3$ and $BaTiO_3$, respectively. It is clear from Figs 7 and 8 that the peaks of PVDF are significant in

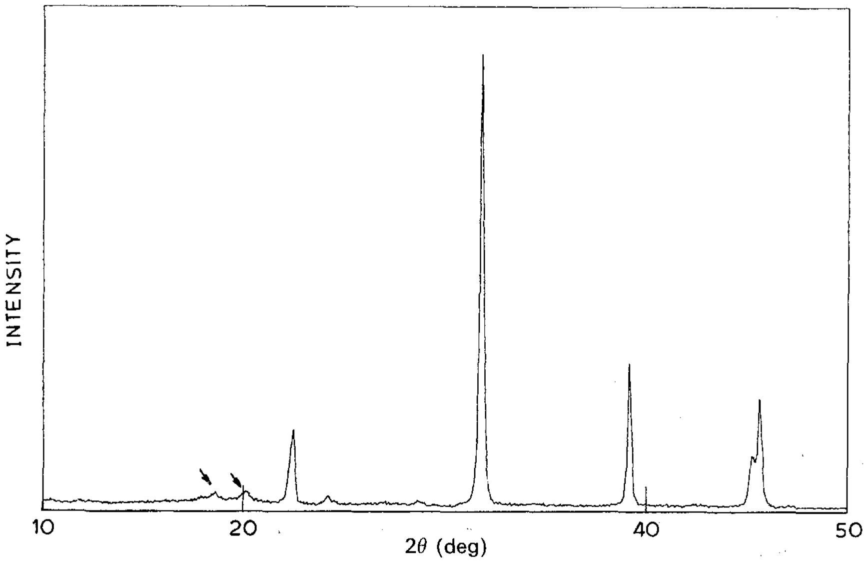

Figure 7 XRD pattern of $BaTiO_3$–PVDF composite of 50 wt % $BaTiO_3$.

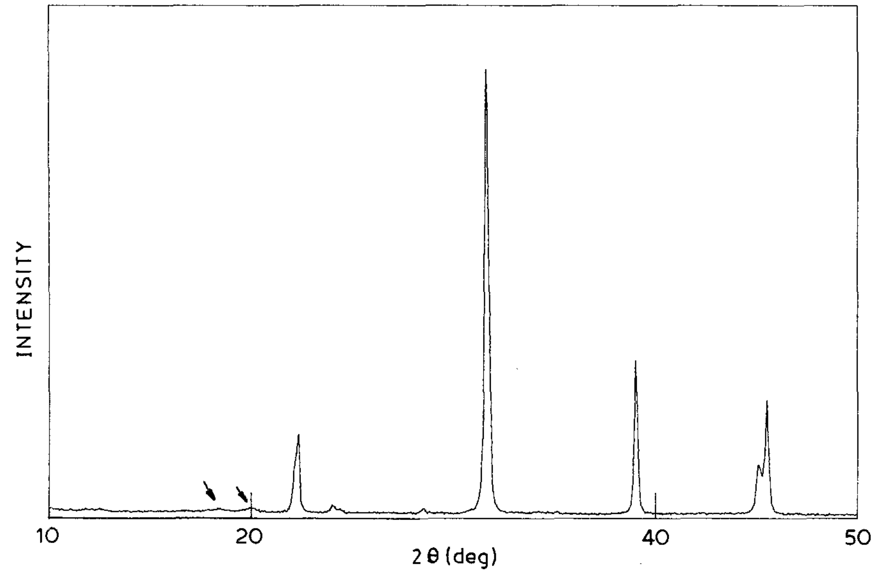

Figure 8 XRD pattern of $BaTiO_3$–PVDF composite of 70 wt % $BaTiO_3$.

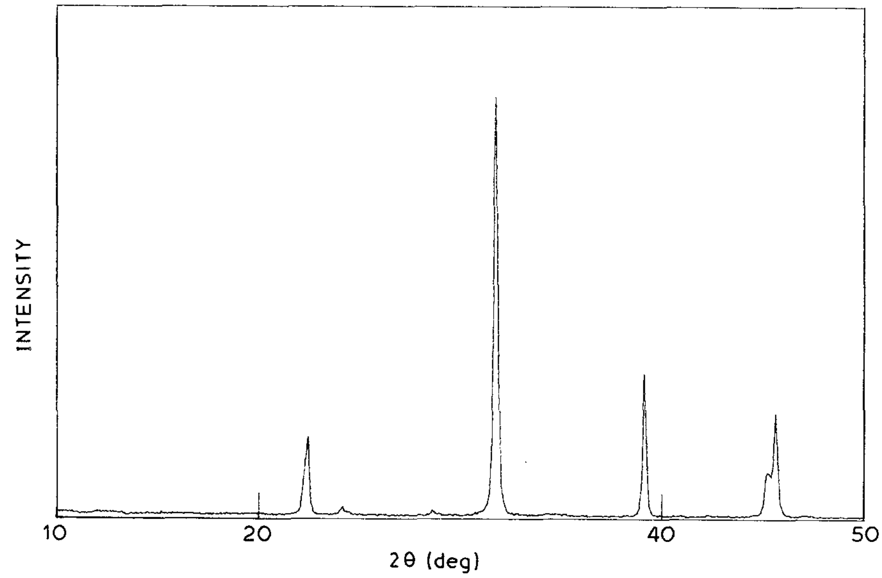

Figure 9 XRD pattern of $BaTiO_3$.

50 wt % and are extremely low in 70 wt % $BaTiO_3$ composites. From this, what we can infer is that at higher weight fractions of $BaTiO_3$, i.e. from 70 wt % onwards, the PVDF does not have any significant influence on any property of the composite. This means that the dielectric behaviour of composites has a significant influence of PVDF in addition to the effect of $BaTiO_3$ upto 50 wt % $BaTiO_3$, and the influence of PVDF is not at all significant at higher weight fractions of $BaTiO_3$. This can be further extended as relaxation peaks of PVDF are very difficult to see at higher weight fractions of $BaTiO_3$.

Also we have shown in our papers [12, 13] that at lower weight fractions of $BaTiO_3$, PVDF has formed an insulating layer over the $BaTiO_3$ grains and this effect is not at all significant at higher weight fractions of $BaTiO_3$, where the grains are clearly seen.

4. Conclusions

At lower weight fractions of $BaTiO_3$ (i.e. upto 50%) PVDF has a significant influence on the dielectric behaviour of the composites, which gradually decreases at higher weight fractions of $BaTiO_3$. At lower frequencies (upto 1 kHz) conduction currents dominate the domain contribution and at higher frequencies (around 10 MHz) a domain wall contribution starts, but these contributions are influenced by the effect of PVDF at lower weight fractions of $BaTiO_3$ which is not significant at higher weight fractions. From the XRD studies it has also been shown that the influence of PVDF is significant at lower weight fractions of $BaTiO_3$, and is insignificant at higher weight fractions.

References

1. C. MURALIDHAR and P. K. C. PILLAI, *IEEE Trans. Electl Insul.* **EI-21** (1986) 501.
2. *Idem, J. Mater. Sci. Lett.* **6** (1987) 346.
3. B. CHERQAOUI, J. GUILLET and G. SAYTRE, *Makromol. Chem. Rapid Commun.* **6** (1985) 133.
4. M. TAKEUCHI, Y. MIYAMOTO and H. NAGASAKA, *Jpn. J. Appl. Phys. Suppl.* **24** (1985) 451.
5. H. THOMANN and H. HEYDRICH, *Ferroelectrics* **7** (1974) 357.
6. D. K. Das GUPTA and K. DOUGHTY, in Proceedings of 4th International Conference on Dielectric Materials, Measurements and Applications. IEE Conference Proc. No. 239, 1904, Lancaster, England, September 1984, p. 164.
7. T. FURUKAWA and E. FUKADA, *Jpn. J. Appl. Phys.* **16** (1977) 453.
8. F. FURUKAWA, K. ISHIDA and E. FUKADA, *J. Appl. Phys.* **50** (1979) 4904.

9. S. Das GUPTA, *J. Appl. Polym. Sci.* **22** (1978) 2383.
10. G. SA-GONG, A. SAFARI, S. J. JANG and R. E. NEWNHAM, *Ferroelectr. Lett.* **5** (1986) 131.
11. C. MURALIDHAR and P. K. C. PILLAI, *J. Mater. Sci.* in press.
12. C. MURALIDHAR, D. SINHA and P. K. C. PILLAI, in Proceedings of 4th National Seminar on Ferroelectrics and Dielectrics. Department of Physics, Indian Institute of Tech., Kharagpur, India, December 1986, p. 46.
13. C. MURALIDHAR and P. K. C. PILLAI, *Mater. Res. Bull.* in press.

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