

Dielectric behaviour of barium titanate (BaTiO_3)/polyvinylidene fluoride (PVDF) composite

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Composite materials are developed by using combinations of phases selected for their best individual properties and put together in a manner designed to show their enhanced properties. They are, therefore, expected to play a vital role in future device design.

Normally polymers have low pyro, piezoelectric coefficients and dielectric constants but have flexibility and lightness, whereas ceramics have high pyro, piezoelectric coefficients and dielectric constants, but are brittle in nature. Thus both have certain restrictions on their use in some specific applications. Therefore, a polymer/ceramic composite would be an ideal replacement for both classes and would have the desirable properties of both materials.

Cherqaoui *et al.* [1] have reported the variation of ϵ' and ϵ'' with frequency for BaTiO_3 /PVDF composite at different volume fractions. In our earlier work [2], the variation of ϵ' and ϵ'' with frequency produced by changing the weight fraction of BaTiO_3 in BaTiO_3 /PVDF composite, has been studied and it was found that the composite with 70 wt % fraction of BaTiO_3 gave $\epsilon' = 133$ at 10 Hz and 30°C. As little work has been reported on the dielectric behaviour of BaTiO_3 /PVDF composite, we felt a detailed study of it to understand the various mechanisms involved was desirable.

The composite sample was prepared by a solvent cast method and aluminium electrodes of area of 1.22 cm² were vacuum deposited on both sides of the film as explained elsewhere [2]. Measurements of ϵ' and $\tan \delta$ were made at frequencies ranging from 10 to 10⁷ Hz using a Hewlett Packard (HP4192A) LF impedance analyser in the temperature range 30 to 190°C.

Figs 1 and 2 show the temperature dependence of ϵ' and $\tan \delta$ of the unpoled BaTiO_3 /PVDF composite with 70 wt % fraction of BaTiO_3 at different frequencies in the temperature range 30 to 190°C. From Fig. 1 it is clear that the rise in ϵ' with increase in temperature is comparatively large at low frequencies up to 1 kHz, but the rise in ϵ' with increase in temperature was not significant at frequencies from 10 kHz to 1 MHz. However, the magnitude of ϵ' again considerably increased at 10 MHz. Also no Curie peaks have been observed (also clear from Fig. 1) and hence there is no abrupt change in the dielectric behaviour of the composite. The absence of Curie peaks can be explained as follows. Because of the ultra-fine particle size of BaTiO_3 (about 1 μm), there is an increasingly important surface effect in which the polarization that results from the tetragonal deformation is locked. This locked-in deformation persists to temperatures

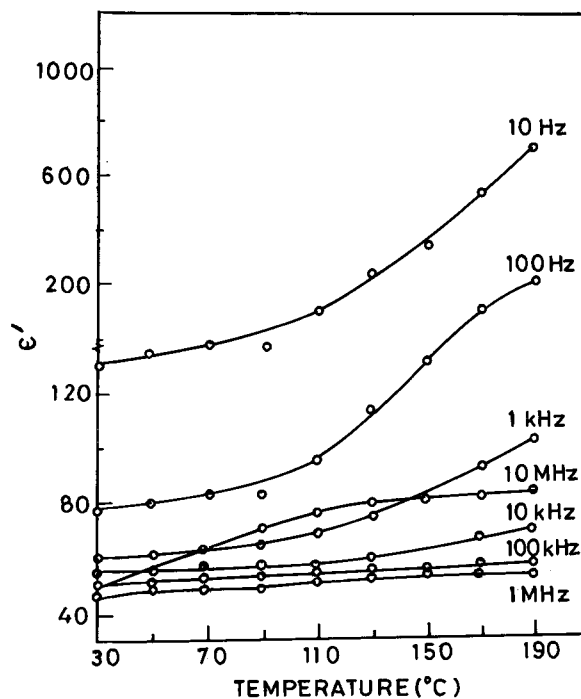


Figure 1 Temperature dependence of ϵ' of BaTiO_3 /PVDF composite with 70 wt % fraction of BaTiO_3 at different frequencies.

far in excess of the usual Curie point and hence the Curie peak is suppressed in the composite. It has been found that the composite also has the off-valency additive effect which is the substitution of O^{2-} by F^- [3]. In the vicinity of a valency defect, the symmetry of the lattice is disturbed, and certain of the possible orientations of the spontaneous polarization will be preferred locally. The variation from point to point of the amount and direction of the disturbing field smears out the Curie point. As the composite experiences both off-valency additive and ultra-fine particle size effects, the dielectric constant peak is nearly washed out. A similar type of a nearly vanishing dielectric constant peak was found in a BaTiO_3 body made of ultra-pure fine-grained material with an admixture of Fe_2O_3 involving both off-valency and fine-grain size effects [3, 4].

From Figs 1 and 2, the rise in ϵ' and $\tan \delta$ with temperature at low frequencies up to 1 kHz can be seen to be due to the free orientation of domains and also to the increase in inhomogeneous conduction which arises from the interfacial polarization. Fig. 3 shows the hysteresis loop of the same composite at 30°C for a sinusoidal field of 15 kV cm⁻¹ at 60 Hz. From Fig. 3 it is clear that the losses at low frequencies up to 1 kHz are mainly attributed to inhomogeneous

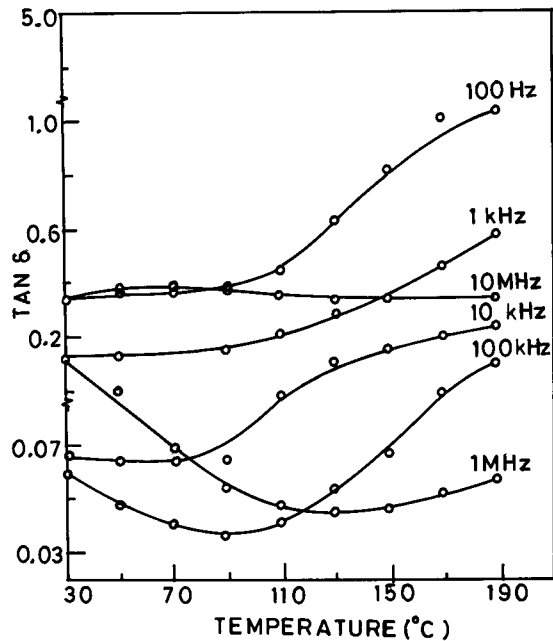


Figure 2 Temperature dependence of $\tan \delta$ of $\text{BaTiO}_3/\text{PVDF}$ composite with 70 wt % fraction of BaTiO_3 at different frequencies.

conduction which arises because of interfacial polarization, as the area of the loop was very small, i.e. at low frequencies conduction losses dominated the domain losses. This is also clear from Fig. 2: the values of $\tan \delta$ are high at low frequencies up to 1 kHz and are very low at frequencies from 10 kHz to 1 MHz. A similar type of conduction loss dominating the ferroelectric losses was observed in Fe_2O_3 -doped BaTiO_3 by Thomann and Heydrich [5]. The rise in ϵ' with temperature is not very significant at frequencies of 10, 100 kHz and 1 MHz and also the values of $\tan \delta$ are comparatively low, which indicates that the losses are mainly from domains. The rise in ϵ' at 10 MHz can be attributed to the domain-wall motion whose natural frequency coincides with the frequency of the applied field which, in effect, gives rise to dielectric dispersion near the GHz region. This is also clear from Fig. 2, the value of $\tan \delta$ again increased at 10 MHz.

Figs 4 and 5 show the frequency dependence of ϵ' and $\tan \delta$ of the composite at different temperatures. From Fig. 4 it is clear that ϵ' decreases with increase in frequency, reaches a minimum at 1 MHz, and thereafter increases with frequency which clearly shows the domain-wall motion as explained earlier. This is also clear from Fig. 5 where the loss again significantly

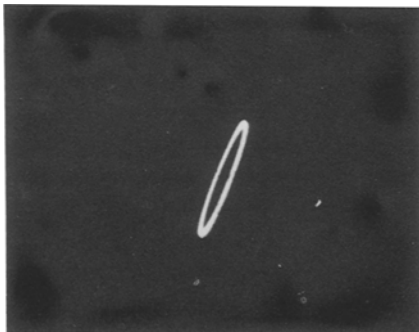


Figure 3 Hysteresis loop of $\text{BaTiO}_3/\text{PVDF}$ composite with 70 wt % fraction of BaTiO_3 at 15 kV cm^{-1} and 60 Hz. Tips of loop are $0.12 \mu\text{C cm}^{-2}$ and 15 kV cm^{-1} .

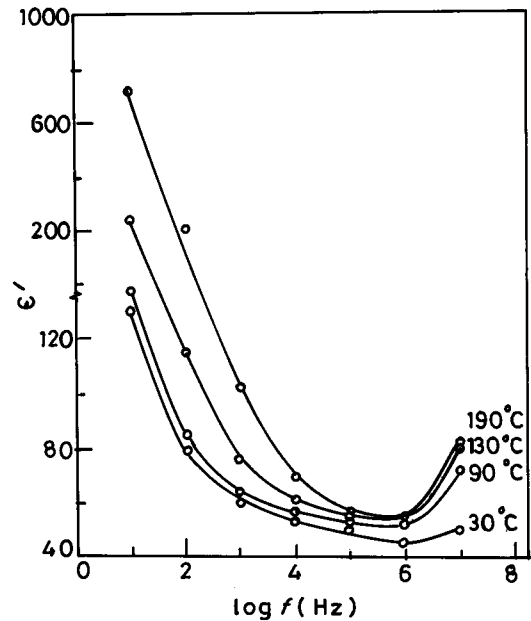


Figure 4 Frequency dependence of ϵ' of $\text{BaTiO}_3/\text{PVDF}$ composite with 70 wt % fraction of BaTiO_3 at different temperatures.

increased after 1 MHz. At low frequencies below 1 kHz, the contribution comes from domains and inhomogeneous conductivity which arises due to interfacial polarization. The losses are also relatively high below 1 kHz, which can be seen clearly from Fig. 5. At low frequencies the conduction losses dominated the domain losses as explained earlier. The losses at frequencies of 10, 100 kHz and 1 MHz are domain losses, reaching a minimum between the above extremes and the same is also true in the case of the frequency dependence of ϵ' . From Figs 4 and 5 it is clear that as the temperature increases, the rise in ϵ' and $\tan \delta$ below 1 kHz is due to the free orientation of domains and is also due to the increase in inhomogeneous conductivity which arises because of interfacial polarization. In addition, the gradual rise in ϵ'

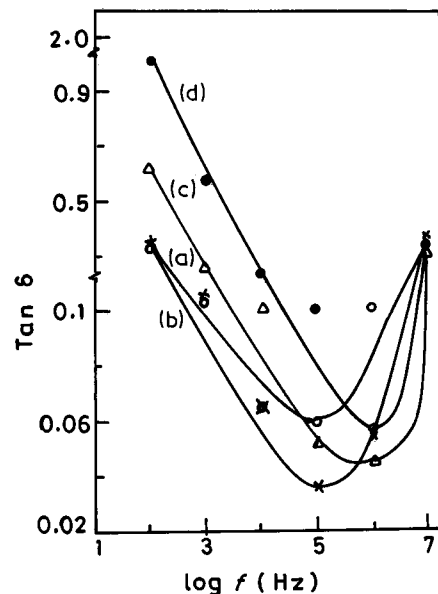


Figure 5 Frequency dependence of $\tan \delta$ of $\text{BaTiO}_3/\text{PVDF}$ composite with 70 wt % fraction of BaTiO_3 at different temperatures. (a) 30°C , (b) 90°C , (c) 130°C , (d) 190°C .

above 1 MHz with increase in temperature is due to the ease of domain-wall motion.

In conclusion, the Curie peak is nearly washed out in the composite because of the combined effects of off-valency additive and ultra-fine particle size. ϵ' increased above 1 MHz because of domain-wall motion. At low frequencies below 1 kHz conduction losses dominated the domain losses. The behaviour of ϵ' and $\tan \delta$ at low frequencies below 1 kHz is attributed to domain motion and inhomogeneous conductivity, and that at high frequencies above 1 MHz is attributed to domain-wall motion.

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