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Charge-field hysteresis of $BaTiO_3$: PVDF composites

R. SHARMA, I. P. SINGH, A. K. TRIPATHI*, P. K. C. PILLAI*
*I. D. D. Centre, and *Department of Physics, Indian Institute of technology, New Delhi, India*

Hysteresis phenomena in $BaTiO_3$: PVDF composites with different weight fractions of $BaTiO_3$ and PVDF were studied in the temperature range 20–180 °C. A sinusoidal electric field of up to 100 $kV\,\mu m^{-1}$ at 50 Hz was used. The saturation polarization, P_{sat}, remanant polarization, P_r, and coercive field, E_c, were observed to increase with increasing ceramic content of the composite samples. An increase of polarization with temperature was observed for all composites up to 80 °C. This has been explained on the basis of an increase in the conductivity of the PVDF phase.

1. Introduction

Over the last decade, piezoelectric and pyroelectric composites based on polymers and electroceramics have received much attention [1–3]. This is mainly due to the fact that enhancement of properties such as pyroelectric and piezoelectric sensitivities, together with low density and high flexibility, can be achieved in ceramic/polymer composites.

Most of the research work reported on polymer/ceramic composites deals with the manipulation of ceramic content, composite design, and poling technique, in order to achieve better piezoelectric and hydrostatic sensitivity. But very little work has been done on the hysteresis phenomena in ceramic polymer composites [4, 5]. Study of the hysteresis loop furnishes information on the dynamic polarizability and is an important property of ferroelectric materials. The present paper describes the hysteresis phenomena in $BaTiO_3$: PVDF composites for different weight fractions of $BaTiO_3$ in a PVDF matrix.

2. Experimental procedure

2.1. sample preparation

Composite samples in the form of 200 μm thick sheets were prepared by hot rolling at a temperature of 165 °C. Because it is difficult to incorporate more than 80% by weight of filler ($BaTiO_3$) by this technique, composites with 90% $BaTiO_3$ (9BT) were made by hot pressing their homogeneous mixture at 165 °C. Hot-pressed pellets were polished, using emery paper; the thickness of a hot-pressed pellet was 650 μm. Pure $BaTiO_3$ Pallets (PBT) were made by adding 2% by weight of Polyvinyl alcohol as binder. $BaTiO_3$ pellets were sintered at 1250 °C for 1 h; the thickness of these pellets was 1 mm. The circular electrodes were formed using air-drying silver paint on both surfaces of the samples.

2.2. Measurements

A circuit similar to a Sawer–Tower circuit [6], was used for hysteresis measurements. Samples were kept in an oil bath in order to ensure uniform heating and to avoid air breakdown at high electric fields. Loops were traced using an oscilloscope (Kikusi-Com 7060). Readings of saturation polarization, P_{sat}, remanant polarization, P_r, and coercive field, E_c, were measured directly from the oscilloscope using a digital readout.

3. Results and discussion

Fig. 1 shows the hysteresis loops of composite samples 7BT, 8BT, 9BT (having 70%, 80% and 90% $BaTiO_3$ content) and PBT sample. Samples with less than 70% weight content of $BaTiO_3$ did not show a proper hysteresis loop. Even Sample 7BT showed a hysteresis loop with a very small open area. It may also be observed from this figure that as the ceramic content in the sample increases, the loops become better in shape. But no saturation polarization was observed for the field applied. Hence the maximum observed polarization has been termed P_{sat} in the case of composites.

From this figure it can also be seen that the shape of the hysteresis loop for pure barium titanate is different from that of the composites. In a barium titanate sample, when the applied field reverses its direction, an initial spike is observed followed by a smooth-humped curve. Such behaviour is usually observed in switching transients of ferroelectrics when the applied field is large (greater than 1.6 $kV\,cm^{-1}$ for $BaTiO_3$) [7]. This initial spike is attributed to charging of the linear component of dielectric and circuit capacitances. The smooth-humped curve results because of the switching of the ferroelectric component [7]. Such behaviour has not been observed for composites. This could be due to the lowering of the effective field on $BaTiO_3$ by the low-permittivity polymer matrix surrounding it [8].

The values of saturation polarization, P_{sat}, remanant polarization, P_r, and coercive field, E_c, for different samples are listed in Table I. It may be seen

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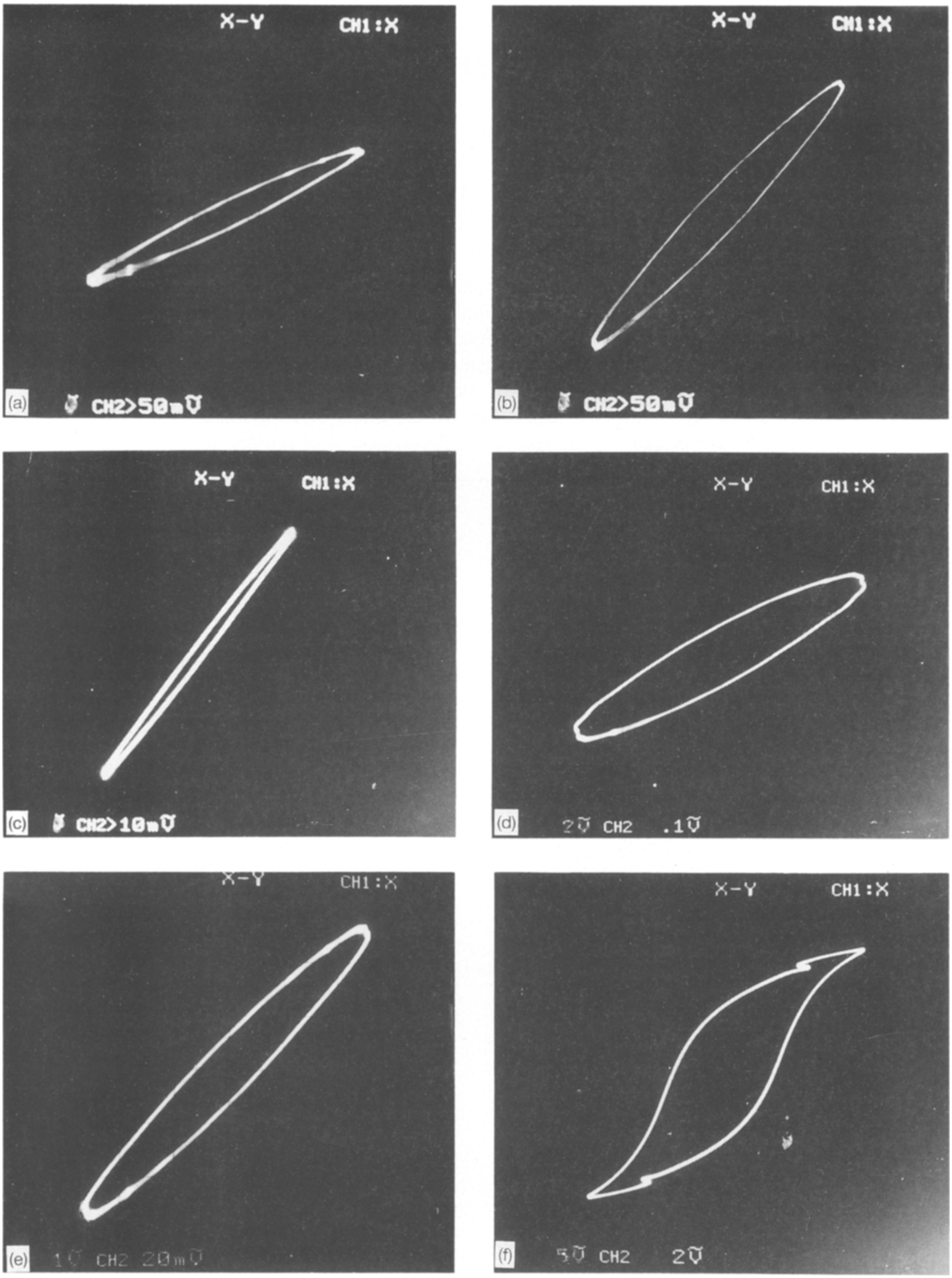

Figure 1 Hysteresis loops for 7BT, 8BT, 9BT and PBT at 20 °C. (a) 7BT at $E_{\mathrm{app}} = 47.6\ \mathrm{kV\,cm^{-1}}$, (b) 8BT at $E_{\mathrm{app}} = 47.6\ \mathrm{kV\,cm^{-1}}$, (c) 8BT at $E_{\mathrm{app}} = 12.4\ \mathrm{kV\,cm^{-1}}$, (d) 9BT at $E_{\mathrm{app}} = 12.4\ \mathrm{kV\,cm^{-1}}$, (e) 9BT at $E_{\mathrm{app}} = 5.7\ \mathrm{kV\,cm^{-1}}$, (f) 9BT at $E_{\mathrm{app}} = 5.9\ \mathrm{kV\,cm^{-1}}$.

that values of P_{sat}, P_{r} and E_{c} increase with increasing ceramic content in the sample. This could be due to the fact that $BaTiO_3$ has a higher polarization. A comparison of these values for different composites reveals that the relative increase in values of P_{sat} and P_{r} is higher when the ceramic percentage is increased from 80% to 90% compared to the increase corresponding to the increase of $BaTiO_3$ content from 70% to 80%. Similar results were reported by Sinha and Pillai [5] for PZT:PVDF composites, and have been explained

TABLE I Values of P_{sat}, P_r and E_c for various samples

Sample	E_{app} (kV cm^{-1})	P_{sat} (μc cm^{-2})	P_r (μc cm^{-2})	E_c (kV cm^{-1})
7BT	47.6	0.145	0.030	11.4
8BT	12.4	0.06	0.005	1.3
	47.6	0.30	0.06	12.9
	67.6	0.51	0.15	19.2
	87.6	0.73	0.24	29.2
9BT	12.4	1.29	0.48	9.0
	22.9	0.36	0.097	3.4
	5.7	0.13	0.037	1.4
PBT	5.9	11.6	6.3	2.1

on the basis of improved connectivity of the ceramic phase and morphological modifications of PVDF under the influence of the ceramic phase. However, even for Sample 9BT, the absolute values of P_{sat} and P_r are substantially lower than that of pure barium titanate. This may be explained on the basis of an increase in $BaTiO_3$ grain size as a consequence of sintering. Moreover, the electric field effective on ceramic particles is lowered considerably owing to the presence of low permittivity PVDF in composites.

Figs 2–4 show the temperature variation of P_{sat}, P_r and E_c for 8BT and 9BT samples and pure $BaTiO_3$ pellets, respectively. The increase of P_{sat} and P_r with

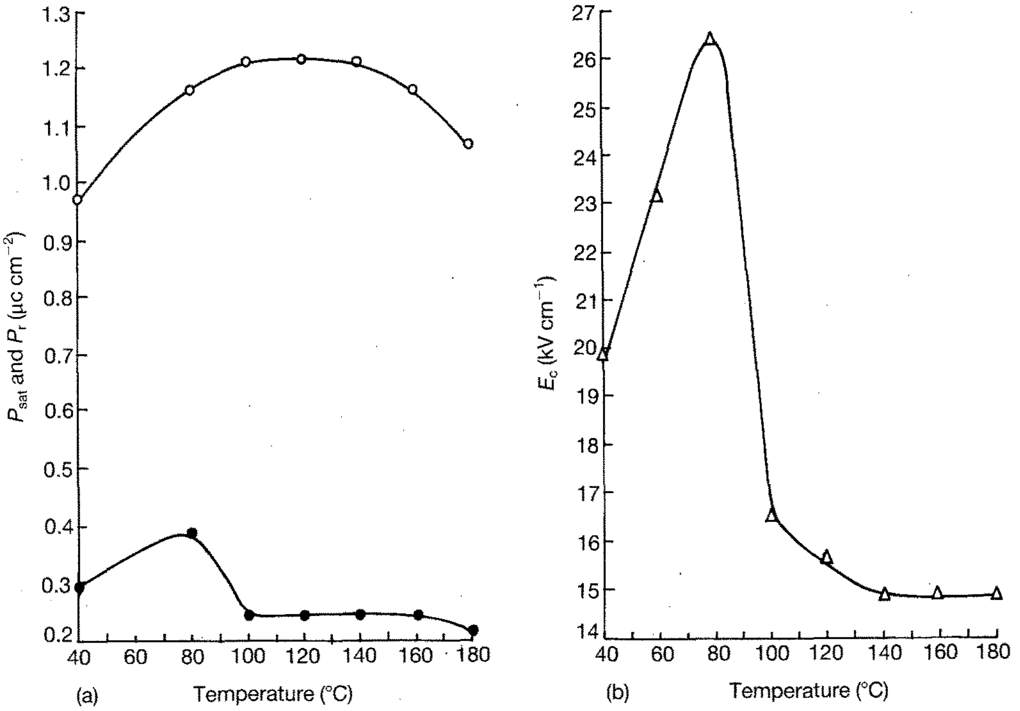

Figure 2 Temperature variation of hysteresis parameters for 8BT (E_{app} = 72.2 kV cm^{-1}): (a) (○) P_{sat} and (●) P_r, (b) E_c.

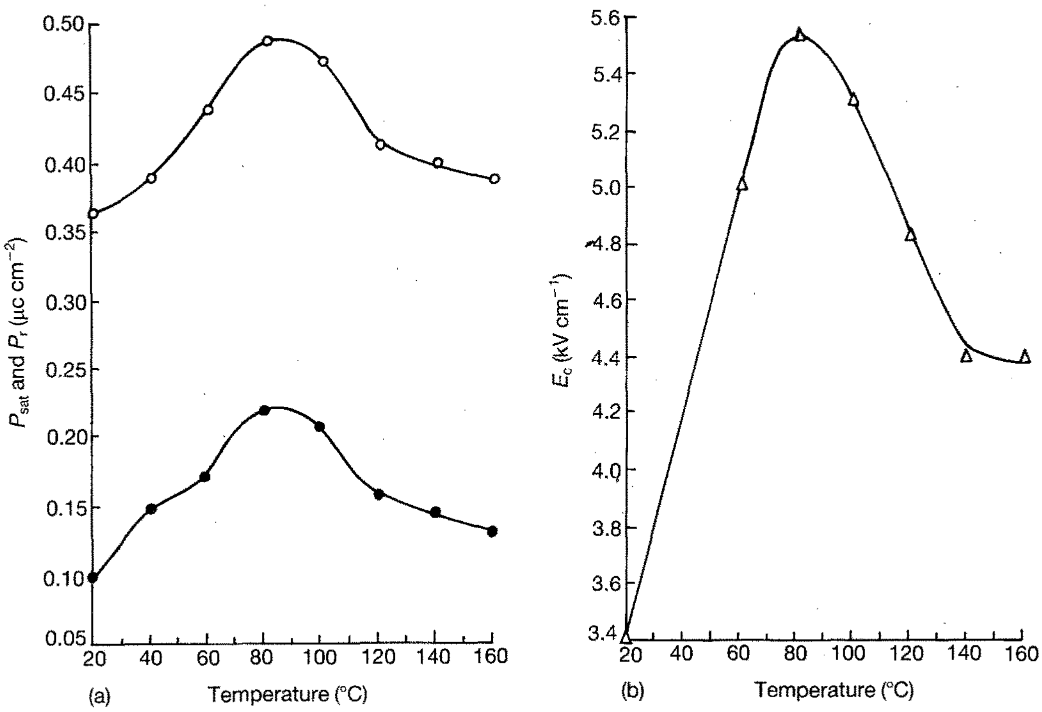

Figure 3 Temperature variation of hysteresis parameters for 9BT (E_{app} = 12.7 kV cm^{-1}): (a) (○) P_{sat} and (●) P_r, (b) E_c.

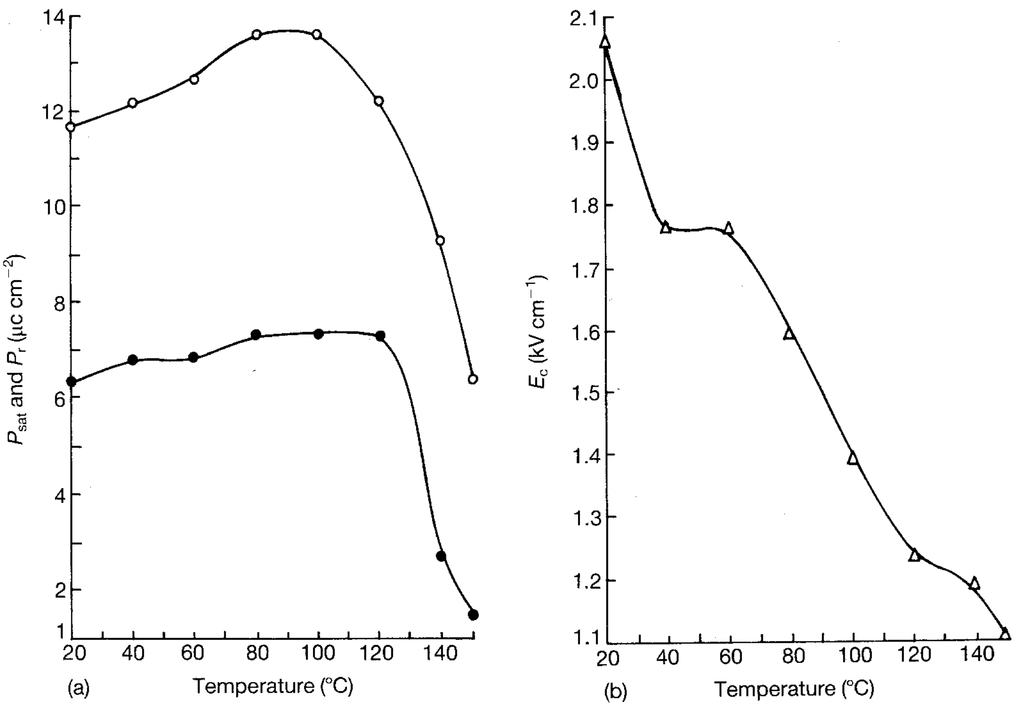

Figure 4 Temperature variation of hysteresis parameters for PBT ($E_{app} = 5.9$ kV cm^{-1}): (a) (○) P_{sat} and (●) P_r, (b) E_c.

temperature, for composites, is explained on the basis of an increase in the conductivity of the PVDF phase. At low temperatures, PVDF forms an insulating layer around $BaTiO_3$, resulting in a considerable reduction of the electric field acting on these grains. However, as the temperature increases, the conductivity of the polymer increases. This leads to application of a higher electric field on ceramic particles, resulting in the increase of P_{sat} and P_r. The decrease in polarization at higher temperatures is observed for composites as well as the pure $BaTiO_3$ sample. This is in accordance with the temperature behaviour of the polarization of ferroelectrics in general [7]. Figs 2 and 3 show an initial increase of E_c with temperature up to 80 °C, followed by a subsequent decrease. The initial increase of E_c corresponds to an increased remanant polarization in the sample: the higher the remanant polarization, the higher will be the electric field required to switch this polarization. The subsequent decrease of E_c is due to a decrease in polarization and increased flexibility of dipoles at higher temperatures.

The variation of P_{sat}, P_r and E_c with temperature for pure $BaTiO_3$ is shown in Fig. 4. Here P_{sat} increases only slightly, while P_r is constant up to 100 °C. Above 100 °C, the polarization decreases with temperature and becomes very low at 140 °C. This may be attributed to a Curie transition of $BaTiO_3$ around this temperature [7]. For ferroelectric materials, the hysteresis loop parameters (P_{sat}, P_r and E_c) are a function of the temperature. Specifically they decrease to zero as the temperature approaches the Curie point. The rate at which the transition occurs is indicative of the type of phase transition. For mixed-phase ceramics, the transition is of a diffused kind, wherein P_r and E_c decrease gradually with temperature [7]. It can be seen from Fig. 4 that E_c decreases with temperature, as expected.

4. Conclusion

From the studies presented here it may be concluded that P_r, P_{sat} and E_c increase with increasing $BaTiO_3$ content in the samples. The low values of P_r and P_{sat} for composites are due to the reduced electric field acting on the ceramic. In addition, P_r and P_{sat} increase with temperature up to 80 °C.

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