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Photoelectret and electrophotographic properties of barium titanate–polyvinylidene fluoride composite film

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Photoferroelectric barium titanate ($BaTiO_3$)–polyvinylidene fluoride (PVDF) composite films in the ratio 70:30 are found to possess good photosensitivity in the visible region of the spectrum. Results on investigations of charge generation, trapping, recombination, discharge and retention properties of the composite film are presented in this paper. Photoinduced polarization is obtained in a $BaTiO_3$–PVDF composite film by the simultaneous application of a d.c. field and illumination from an argon-ion laser or by white light. The dark (photo) polarization and the dark (photo) depolarization current decay characteristics of the polarized films have been studied under different experimental conditions. The studies show that the composite film retains good polarization for a fairly long time in the dark condition, and the magnitude of the depolarization current is comparable with that of $BaTiO_3$ single crystal. Under illumination, the decay is fast enough to make use of the film for electro-photographic applications.

1. Introduction

Composite materials have been attracting a great deal of attention in recent years because of their superior mechanical, thermal, electrical and fabrication properties compared with their individual components. Ceramic–polymer composites have been the subject of investigation for their applications in transducers, dielectric memory and sensors [1–4]. The properties of polymeric composites are reviewed by Newnham [5, 6] and Cherqouet *et al.* [7]. Muralidhar and Pillai [8, 9] have studied the dielectric properties of $BaTiO_3$–PVDF composites in 0–3 connectivity pattern for a frequency range from 100 Hz to 5 MHz at ambient temperature by changing the volume/weight fraction of $BaTiO_3$. Muralidhar and Pillai have observed that the dielectric behaviour of the composite is significantly influenced by the magnitude of PVDF present in the composite. They have also studied the temperature dependence of resistivity and hysteresis behaviour of the $BaTiO_3$–PVDF composites [10, 11]. Composite samples in the 0–3 connectivity pattern need to be poled at around 100 °C for 30 min to 1 h under an external electric field of about $100\ \mathrm{kV\,cm^{-1}}$ and above to show any significant piezoelectricity. They have also observed that the dielectric behaviour of the composite is influenced by that of the PVDF for lower concentrations of $BaTiO_3$ in the composite sample.

Composite materials are expected to play a vital role in future device applications. Polymer–ceramic composites would be ideal replacements for both polymers and ceramics, as the composites would have the flexibility and light weight of the polymers and the high pyroelectric, piezoelectric and dielectric constants of the ceramics. In earlier work, it was shown that $BaTiO_3$–PVDF composites with 70% weight fraction of $BaTiO_3$ have high pyroelectric and dielectric constants [12, 13]. The dielectric constant of PVDF polymer film is strongly dependent on the fabrication process, as PVDF exists in several crystalline phases and the predominance of individual phases can be controlled by the film fabrication process [14].

$BaTiO_3$ is a photoferroelectric material which changes its ferroelectric properties when optically excited [15]. The existence of photo-stimulated phase transitions in ferroelectric materials is of fundamental interest. Although some work has been reported on the dielectric, pyroelectric, ferroelectric and piezoelectric properties of $BaTiO_3$–PVDF composites, no report has yet been published on their electret and electro-photographic properties. The charge carriers (electrons and holes) originate from defects or impurities in the material which migrate from one site to another upon illumination. The creation of photo-excited free carriers, their displacement under the influence of an external field, and subsequent localization of these carriers at various trapping sites are important in understanding the mechanism of polarization in these classes of materials. Therefore, studies on the dark(photo)-induced polarization and dark(photo)-induced depolarization properties in this composite material and their possible applications in electrophotography as a photoreceptor are undertaken in this paper.

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2. Experimental details

PVDF, obtained from Janssen Chimeiea, Belgium, was dissolved in dimethyl acetamide (DMA) at 70 °C to make a sufficiently vicious solution. Barium titanate powder of about 1 μm particle size was dispersed into the solution and stirred thoroughly to obtain a homogeneously dispersed mixture. Since a composite with 70% weight fraction of $BaTiO_3$ has previously been shown to have desirable properties, a solvent-cast film of 13 μm thickness with this composition was prepared by pouring the solution on to a clean glass plate. These films were dried at 60 °C for 48 h in an oven to remove traces of the solvent. The film was cut into circular pieces of 2 cm diameter, and a circular aluminium electrode of 1 cm^2 was vacuum-deposited on one of the film surfaces for obtaining better electrical contact. The prepared sample was sandwiched in between two transparent conducting electrodes and mounted in a Teflon sample holder assembly. The assembly was positioned in front of a 200 W 110 V tungsten filament lamp. An infrared filter was mounted in front of the lamp to reduce heating of the film by long-wavelength radiation. The sample could also be illuminated by an argon-ion laser beam at 514.5 nm wavelength. The transparent conducting electrodes were connected either to a variable high-voltage d.c. supply to polarize the sample or a Keithly picoammeter (model 485) to measure the discharging current using a two-way switch. The output of the picoammeter was connected to a Hewlett Packard computer (model 9836U) for automatic recording of the discharging current and reduction of data (Fig. 1).

A d.c. voltage of appropriate strength was applied along the crystal axis for a known duration to induce volume polarization in the sample. The sample was simultaneously illuminated with either an argon-ion laser beam or with white light at a known intensity. This enabled us to study the photo-induced polarization and subsequent trapping of the charge carriers near to each electrode. At the end of photopolarization the d.c. field was terminated, and the depolarization (discharging) current and charge with time were measured under dark and illumination conditions.

3. Results

Figs 2 and 3 show the photo-depolarization current decay characteristics of the photoelectret $BaTiO_3$–PVDF composite prepared by varying the poling times from 5 to 120 min, applying 78.7 kV cm^{-1} field and irradiating with 0.1 W cm^{-2} white light. The results show that there is a significant increase in the magnitude of the current with increase of poling time. In all cases the current, initially in the nano-ampere range, decays rapidly during the first few minutes and reaches a slower decay rate thereafter. The photo-depolarization current as a function of the poling time for the photoelectret of the composite prepared at different photo-decay times (5 to 120 min) and under the same poling conditions is shown in Fig. 4. The results show that the depolarization current increases with increase of the poling time.

In Fig. 5 the photodecay current is plotted against the poling field. In Fig. 6 the total charge induced is plotted against the poling field. In both cases, the effect of the poling field on the formation of the photoelectret of $BaTiO_3$–PVDF composite is illustrated: the current and the charge yielded during photo-depolarization increase with increase of the poling field. This levels off and becomes gradual with further increases of the poling field. The results show that, to obtain good volume polarization with stability, a field strength of about 64 kV cm^{-1} should be applied across the sample.

Fig. 7 shows the photodecay current as a function of the poling intensity for the composite at different

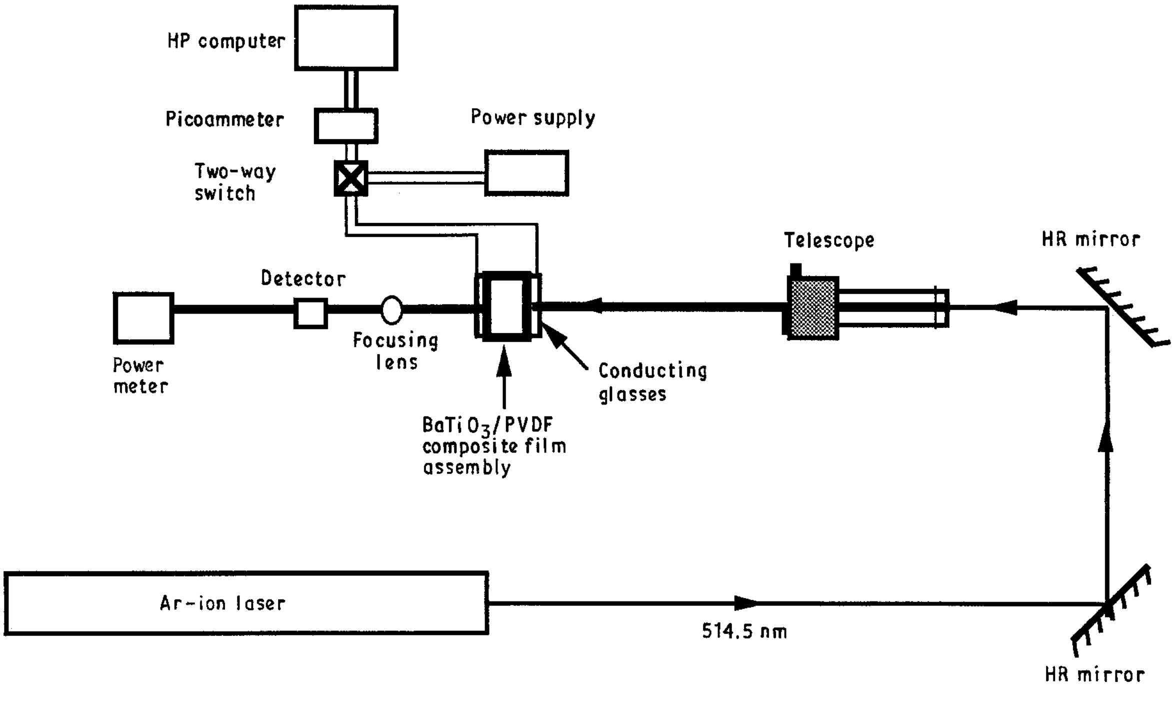

Figure 1 Experimental set-up.

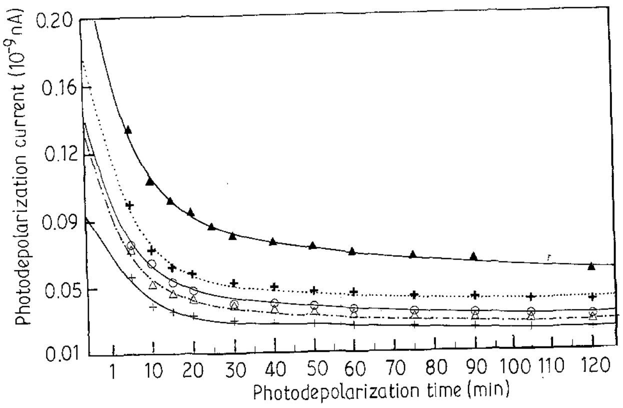

Figure 2 Depolarization current against depolarization time for poling times of (+) 5, (△) 15, (○) 30, (+) 60 and (▲) 120 min, for a photoelectret of $BaTiO_3$–PVDF polarized for 60 min with 78.7 kV cm^{-1} at 65 °F (18 °C) and illuminated with 0.1 W cm^{-2} white light.

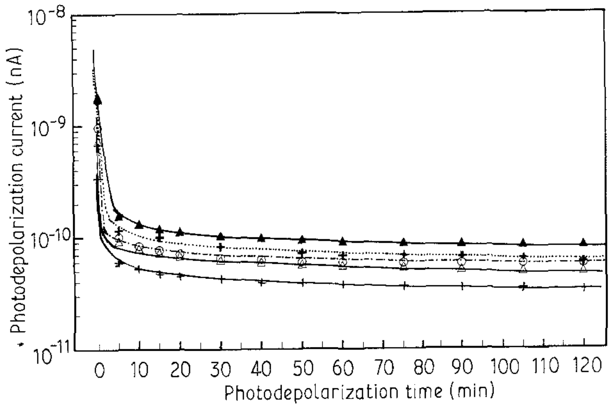

Figure 3 Logarithmic plot of depolarization current against depolarization time for poling field of (+) 16, (△) 32, (○) 47, (+) 63 and (▲) 95 kV cm^{-1}, for a photoelectret of $BaTiO_3$–PVDF polarized for 60 min at 65 °F (18 °C) and illuminated with 0.1 W cm^{-2} white light.

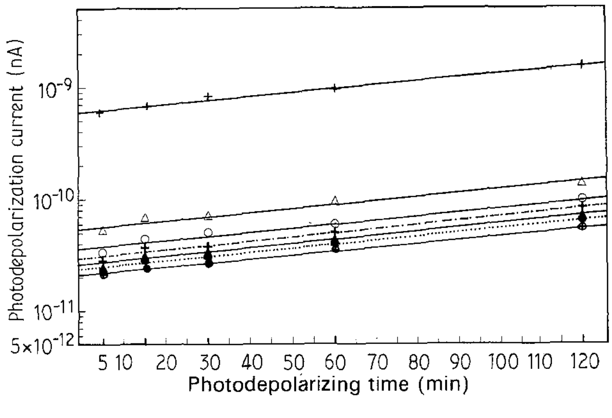

Figure 4 Logarithmic plot of depolarization current against poling time at photodecay time of (+) 1, (△) 5, (○) 15, (+) 30, (▲) 60, (●) 90 and (⊕) 120 min, for a photoelectret of $BaTiO_3$–PVDF polarized with 3 kV (or 78.7 kV cm^{-1}) at 65 °F (18 °C) and illuminated with 0.1 W cm^{-2} white light.

photo-decay times while keeping other poling parameters the same as before. The results show that the photodecay current increases with increase of the illumination intensity.

Fig. 8 shows the current decay for illumination at 0.1 to 0.4 W cm^{-2} with the argon-ion laser (514.5 nm wavelength). Fig. 9 shows that increasing the laser irradiation intensity will yield more depolarization current. Fig. 10 plots the decay current against the poling field at different decay times when the sample is laser-irradiated. Again, the current increases with increase of the poling field and decreases as soon as the external voltage is shorted out.

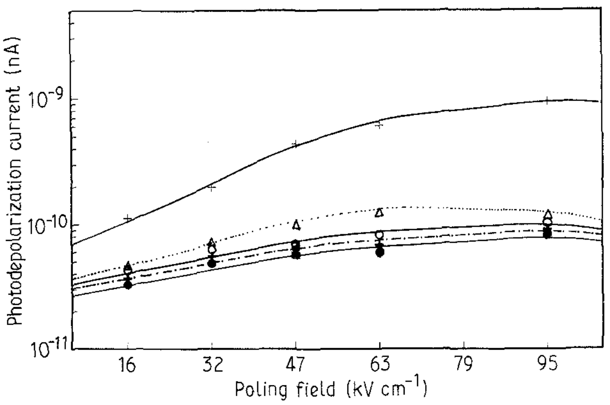

Figure 5 Logarithmic plot of depolarization current against poling field for photodecay time of (+) 1, (△) 15, (○) 30, (+) 60, (▲) 90 and (●) 120 min, for a photoelectret of $BaTiO_3$–PVDF at 65 °F (18 °C) and illuminated with 0.1 W cm^{-2} white light.

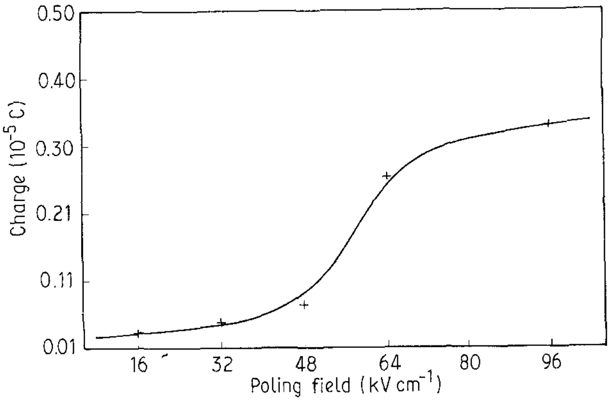

Figure 6 Total charge against poling field for a photoelectret of $BaTiO_3$–PVDF polarized for 60 min at 60 °F (18 °C) and illuminated with 0.1 W cm^{-2} white light.

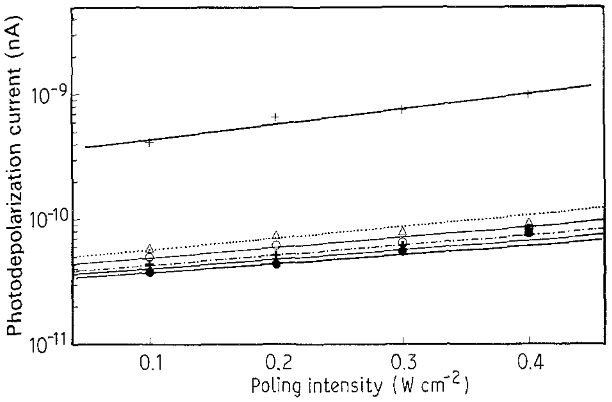

Figure 7 Logarithmic plot of depolarization current against poling intensity for photodecay time of (+) 1, (△) 15, (○) 30, (+) 60, (▲) 90 and (●) 120 min, for a photoelectret of $BaTiO_3$–PVDF polarized for 60 min at 65 °F (18 °C) and illuminated with white light.

Fig. 11 plots the decay current against poling time (15 to 60 min). It shows that more current is generated

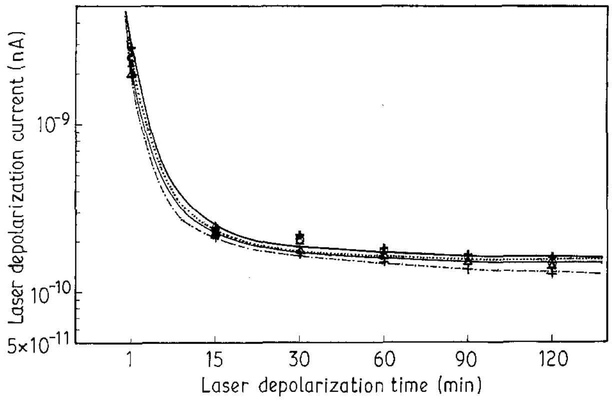

Figure 8 Logarithmic plot of depolarization current against depolarization time for poling intensity (+) 0.1, (△) 0.2, (○) 0.3 and (+) 0.4 W cm^{-2}, for a photoelectret of BaTiO$_3$–PVDF polarized with 78.7 kV cm^{-1} for 60 min at 65 °F (18 °C) (wavelength = 514.5 nm).

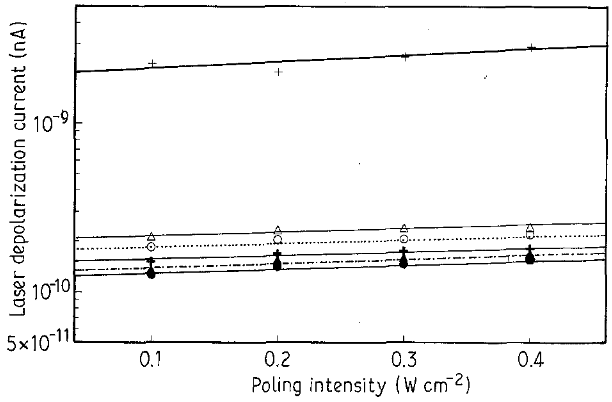

Figure 9 Logarithmic plot of depolarization current against poling intensity for laser decay time (+) 1, (△) 15, (○) 30, (+) 60, (▲) 90 and (●) 120 min, for a photoelectret of BaTiO$_3$–PVDF polarized with 78.7 kV cm^{-1} for 60 min at 65 °F (18 °C) and illuminated with 0.1 W cm^{-2} argon-ion laser (wavelength = 514.5 nm).

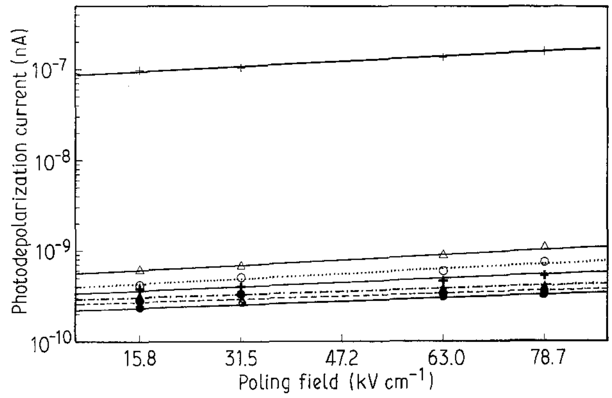

Figure 10 Logarithmic plot of depolarization current against poling field for laser decay time (+) 0, (△) 5, (○) 15, (+) 30, (▲) 60, (●) 90 and (⊕) 120 min, after poling a photoelectret of BaTiO$_3$–PVDF at 65 °F (18 °C) for 5 min and illuminated with 0.1 W cm^{-2} argon-ion laser (wavelength = 514.5 nm).

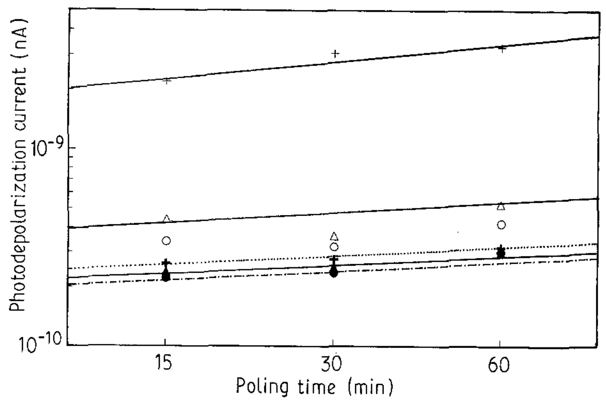

Figure 11 Logarithmic plot of depolarization current against poling time for photodecay time (+) 1, (△) 15, (○) 30, (+) 60, (▲) 90, (●) 120 min, for a photoelectret of BaTiO$_3$–PVDF polarized at 65 'F (18 °C) for 60 min and illuminated with 0.1 W cm^{-2} argon-ion laser (wavelength = 514.5 nm).

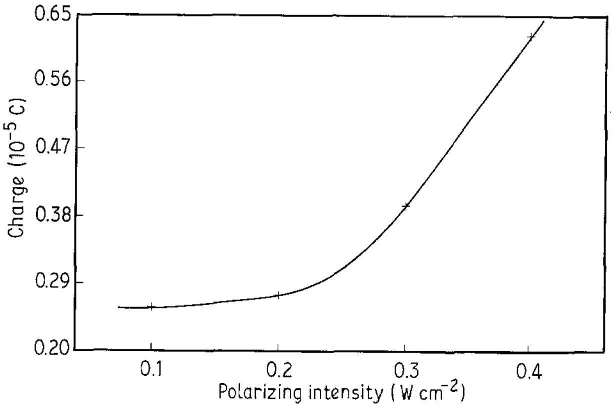

Figure 12 Total charge against poling intensity after poling a photoelectret of BaTiO$_3$–PVDF for 60 min at 65 °F (18 °C) and 78.7 kV cm^{-1} and illuminated with 0.1 W cm^{-2} white light.

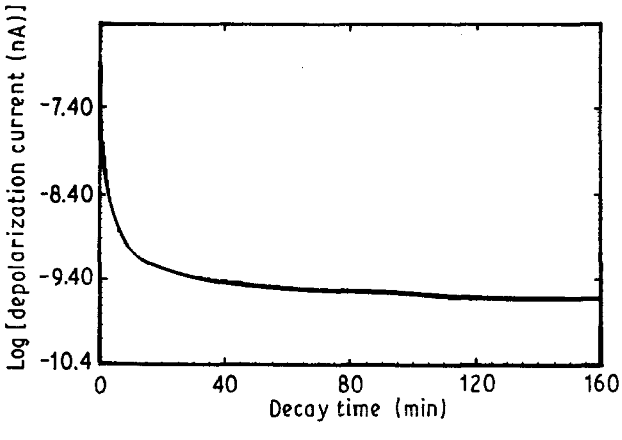

Figure 13 Log of laser depolarization current against laser depolarization time for a photoelectret of BaTiO$_3$ single crystal polarized with 6 kV cm^{-1} for 60 min at 70 °F (21 °C) and illuminated with 0.15 W cm^{-2} argon-ion laser (wavelength = 514.5 nm).

when the sample is polarized longer. Also, as shown in Fig. 12, the total charge yielded after poling for 60 min increases sharply when the sample is illuminated with intensities greater than 0.3 W cm^{-2} for the composite film.

Fig. 13 illustrates the laser-induced depolarization current decaying with time for a BaTiO$_3$ single crystal (6 mm × 5 mm × 5 mm) illuminated by the 514.5 nm argon-ion laser and polarized by an applied 6 kV cm^{-1} field for 60 min. The relationship between the depolarization current and the laser illumination intensity for the same poling voltage and duration is also illustrated in Fig. 14. From the results we can conclude that there exists a similarity between the

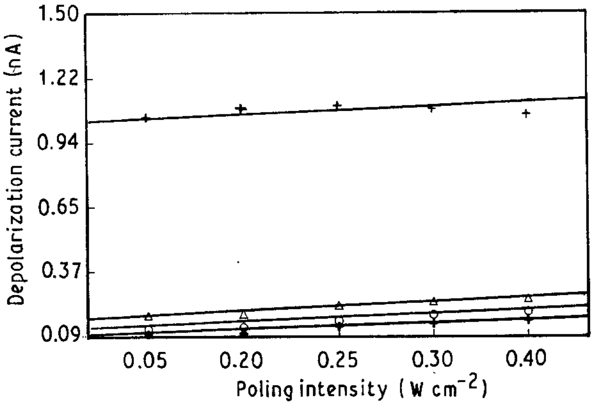

Figure 14 Photodepolarization current against poling intensity for photodecay time (+) 5, (△) 15, (○) 60 and (+) 120 min, for a photoelectret of $BaTiO_3$ single crystal (5 mm thickness) polarized with 6 kV cm^{-1} for 60 min at 70 °F (21 °C).

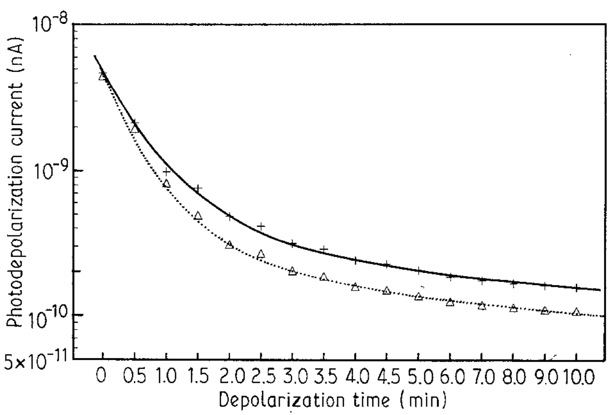

Figure 15 Logarithmic plot of depolarization current against depolarization time for (+) dark polarization/dark depolarization and (△) dark polarization/photodepolarization (0.1 W cm^{-2} white light) for a photoelectret of $BaTiO_3$–PVDF polarized with 78.7 kV cm^{-1} for 60 min at 70 °F (21 °C).

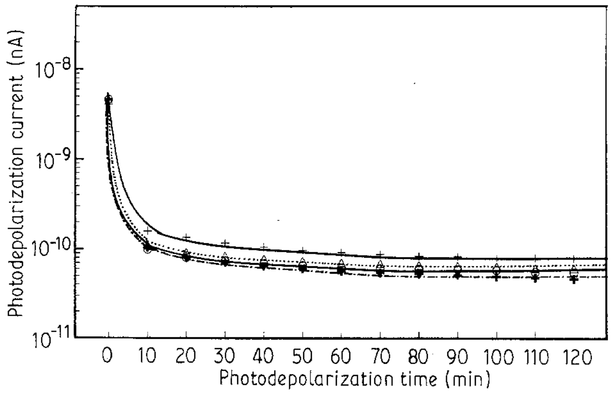

Figure 16 Logarithmic plot of depolarization current against depolarization time for (+) dark polarization/dark depolarization, and for dark polarization/photodepolarization at (△) 0.1, (○) 0.2 and (+) 0.4 W cm^{-2} white light, for a photoelectret of $BaTiO_3$–PVDF polarized with 78.7 kV cm^{-1} for 60 min at 72 °F (21 °C).

$BaTiO_3$ single crystal and the composite film in the generation of photoelectret current (charge).

Fig. 15 shows the current decay characteristics under dark- and photo-depolarization (0.1 W cm^{-2} white light) for the composite prepared by applying 78.7 kV cm^{-1} field for 60 min. The rate of decay for photo-depolarization is faster than for dark-depolarization. This demonstrates that the composite films can be used as a photoreceptor for xerography, particularly in persistent internal-polarization (PIP) electro-photographic applications. Fig. 16 shows that the current generated during photoelectret formation decays faster under reillumination than in the dark, and the decay rate increases with an increase of the illumination intensity.

4. Discussion

When a photoconducting material, such as the composite film, is subjected to an external electric field and simultaneously irradiated, charge carriers are generated when the energy gap of the material is equal to the energy of the illumination radiation, $h\nu$, where ν is the frequency of the radiation. The carriers drift to either side of the material under the influence of the applied d.c. field and are trapped in respective electron and hole trapping centres, thus forming trapped carrier layers. The layers at either side of the sample give rise to a stable internal polarization, and this is generally referred as the photoelectret state. Deep traps in the photoconductor are required for the formation of a stable photoelectret. The trapped charges are usually released by reilluminating the sample with the same polarizing radiation or image light in the electrophotographic mode of application. After polarization, when the sample is kept in the dark, a dark depolarization current is produced as shown in Fig. 15. This is due to thermal excitation of the trapped carriers to the conduction band and the subsequent motion of the carriers under the influence of the internal field [16].

The general behaviour of the depolarization current and charge, as shown in Figs 2, 3, 8, 13 and 16, can be explained on the basis of the existence of shallow and deep trap levels in the composite films. The photorefractive $BaTiO_3$ grains with iron doping are dispersed in the PVDF medium. The composite films possess large numbers of both deep and shallow traps. For shallow traps $E_t < kT$ and for deep traps $E_t > kT$ where E_t is the trap depth, K is Boltzman's constant and T is the absolute temperature. Therefore, the initial rapid decay can be explained by the diffusion and migration of charge carriers and the thermal release of trapped carriers from shallow traps. Since the trapped carriers can gain energy in quanta of kT, the carriers from the deep traps will jump to the next trap levels in steps of kT. Thus, it will take several attempts and a longer time for the carriers to reach the conduction band. Consequently, the current and charge decay will slow down after the initially quick decay. Similarly, the persistence and stability of the depolarization current in the composite film can be explained using the deep-trap process.

The decay of charge accumulated in a photoelectret during reillumination can be estimated using the following equation [17]:

$$\frac{dN}{dt} = -IN\nu\exp\left(-\frac{E_1}{kT_e}\right) + n(m - N)vS_n \quad (1)$$

where N is the number of carriers in the trapping levels that contribute to the photoelectret formation, I

is the intensity of the reillumination, m is the total number of traps available, $\nu = N_e v S_n$ is the attempt-to-escape frequency, E_1 is the trap depth, T_e is the electronic temperature of the sample, n is the number of electrons in the conduction band, v is the thermal velocity of electrons and S_n is the capture cross-section.

During the depolarization process, the second term is small and can be neglected. Therefore N, the number of carriers in the trapping levels that contribute to the photoelectret formation, becomes [18]

$$N = N_s \exp(-a_1 E) \tag{2}$$

where

$$a_1 = \nu \exp(-E_1/kT_e) \tag{3}$$

$$N_s = \frac{J_s M}{j_s - N_c I_p \mu n E_p \exp(-E_1/kT)} \tag{4}$$

and j_s = saturation value of the polarizing current, I_p = intensity of the polarizing radiation, μ = mobility of electrons, E_p = applied electric field and $N_c = 2(2\pi mkT/h^2)^{3/2}$.

The depolarization current during reillumination of the polarized sample can be calculated from the rate equation [19]

$$I\frac{dn}{dx} = -I\frac{dn}{dz} - \frac{d}{dx}\left(n\mu E' - D\frac{dn}{dx}\right) \tag{5}$$

where

$$Z = It = \text{exposure } (t = \text{exposure time}) \tag{6}$$

$$D = kT\mu/e = \text{diffusion coefficient of electrons} \tag{7}$$

$$E' = -Ne/C = \text{internal field due to photoelectret polarization of unit area of cross section and for uniform trapping of electrons in the sample} \tag{8}$$

Thus, the experimental results on current and charge decay observed in the present investigations can be explained generally using the above equations.

The fractional decrease of charge and current during depolarization shows that the composite layer can be a good photoreceptor for electro-photographic and other imaging applications. The electro-photographic (xerographic) processes involve the formation of a latent electrostatic image on a uniformly charged photoreceptor surface and later transference of the image on to a paper or other material with the help of toner particles. The major requirements for a photoreceptor to be a good xerographic material are high dark resistivity, capacity to accept charge, slow dark decay, fast light decay, good contrast potential, and panchromatic spectral sensitivity. The results, shown in Figs 15 and 16, indicate that the dark decay is slower than the photo-decay. Also, there is an 80% decrement of decay current about a minute after terminating polarization. The decay slows down thereafter, and the current persists thereafter. From these characteristics, it can be concluded that the $BaTiO_3$–PVDF composite layer can be used for electro-photographic applications.

5. Conclusions

1. The present study reveals that a $BaTiO_3$–PVDF composite with 70% weight fraction of $BaTiO_3$ is a very good photoelectret material.
2. An overall examination of the dark-decay and photo-decay characteristics under different photoelectret forming and depolarization conditions show that the composite layer can be employed for electro-photographic applications as well as a viable photoreceptor.

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References

1. R. E. NEWNHAM, D. P. SKINNER and L. E. CROSS, *Mater. Res. Bull.* **13** (1970) 525.
2. K. A. KLICKER W. A. SCHULZE and J. V. BIGGERS, *J. Amer. Ceram. Soc.* **6** (1982) L208.
3. K. NAKUGAWA, T. YANAGIDA, H. TOKUTA and T. FUKASE, *Jap. J. Appl. Phys.* **24** Suppl. (24–2) (1985) 479.
4. E. C. GALOCI, D. G. SCHREFFLER, B. P. DELVIN and J. RUNT, *Ferroelectrics* **68** (1986) 109.
5. R. E. NEWNHAM, *Ann. Rev. Mater. Sci.* **16** (1986) 47.
6. *Idem, Ferroelectrics* **68** (1986) 1.
7. B. CHERGAUOI, J. GUILLET and G. SEYTRE, *Makromol. Chem. Rapid Commun.* **6** (1985) 133.
8. C. MURALIDHAR and P. K. C. PILLAI, *IEEE Trans. Elect. Insul.* **E1-21** (1986) 501.
9. *Idem, J. Mater. Sci. Lett.* **6** (1987) 346.
10. *Idem, ibid.* **6** (1987) 349.
11. *Idem, ibid.* **6** (1987) 439.
12. Y. HIGASHIHATA, T. YAGI and J. SAKO, *Ferroelectrics* **68** (1986) 63.
13. T. YAMADA, T. UEDA and K. KITAYAMA, *J. Appl. Phys.* **53** (1982) 4328.
14. RASHMI, G. K. NARULA and P. K. C. PILLAI, *J. Mater. Sci.* **22** (1987) 2006.
15. PUCHI YEH, *J. Opt. Soc. Amer.* 8, **4** (1987) No. 9.
16. V. M. FRIDKIN and I. S. ZHELUDEV, "Photoelectrets and Electrophotographic Process" (Von Nostrand Princeton, New Jersey, 1963) p. 240.
17. P. K. C. PILLAI and K. G. BALAKRISHNAN, *Phys. Rev. B*, **7** (1973) 3131.
18. B. M. GOLOVIN, N. T. KASHUKEEN and V. M. FRIDKIN, *Sov. Phys. Dokl.* **4** (1960) 985.
19. *Idem, ibid.* **4** (1960) 985.

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