

## Transient currents in discharge mode in cellulose acetate:polyvinyl acetate blend films

P K KHARE, R S CHANDOK\* and A P SRIVASTAVA†

Department of Postgraduate Studies and Research in Physics, Rani Durgavati Vishwavidyalaya, Jabalpur 482001, India

\* Shri Guru Tegh Bahadur Khalasa College, Jabalpur 482001, India

\* 39, SBI Colony, SAF Road, Makronia, Sagar 470003, India

MS received 3 September 1994; revised 14 November 1994

**Abstract.** The transient currents measured in discharge mode with cellulose acetate (CA): polyvinyl acetate (PVAc) blend films ( $\approx 20 \mu\text{m}$  thick) as a function of charging field [ $(1.5\text{--}4.5) \times 10^4 \text{ V/cm}$ ], temperatures (323–373 K) and polymer weight ratio (90:10 and 75:25) have been found to follow Curie–von Schweidler law, characterized with two slopes in short and long time regions. Isochronals characteristics (i.e. current/temperature plots at constant times) constructed from these data seemed to reveal a broad peak observed at 363 K. Values of activation energy increase with PAVc content and also with time of observation. Space charge due to trapping of injected charge carriers in energetically distributed traps and induced dipoles created because of the piling up of charge carriers at the phase boundary of heterogeneous structure of blend are considered to account for the observed currents.

**Keywords.** Transient currents; cellulose acetate; polyvinyl acetate; induced dipoles; space charge; plasticization effect.

**PACS Nos** 77·30; 81·40; 81·20

### 1. Introduction

In polymer dielectrics movement of charge carriers has received a good attention because of its importance in science and technology, which include leakage current in electrical insulation [1, 2], charge injection from electrodes which may lead to premature breakdown [3], various forms of photoconduction and of transient pulse drift and induced conductivity. These problems involve the transport and distribution of charged particles which, therefore, be treated as quasi-continuous clouds rather than as individual. However, despite serious efforts [4–6], there remains substantial doubt as to mechanism of charge transport in many insulating polymers which find very wide industrial applications. There are various methods of studying conduction processes [7] which include AC conduction studies, charge particle bombardment, surface voltage decay, trapped charge decay, radiation induced conduction and photo conduction. However, there are uncertainties inherent in each of the above methods. Therefore, fresh attempts were undertaken to study the time dependent dielectric absorption/desorption current flow, following the application of a step voltage.

A systematic study of transient currents can reveal the carrier injection, trapping and polarization processes which may be operative in a dielectric. The knowledge of transient currents is also necessary to discover the true conductivity of the material.

The transient current data can be converted from time to frequency domain by Fourier transformation to give dielectric loss of the material at low frequencies [8]. The time dependent part of the current is due to polarization of the dielectric under the applied electric field. The polarization of polymeric dielectrics may be due to dipolar orientation, accumulation of charge carriers near the electrodes or trapping in the bulk [5]. Under certain conditions additional charge carriers may be provided by injection from the electrodes which also contribute in space charge polarization [9]. Hopping of charge carriers from one localized state to another [10] and tunnelling from electrode to those trap levels in the dielectric which are close to the Fermi level of the electrode metal [4] have been proposed for the transient currents in dielectrics. The process which actually occurs must be determined by considering the variation of the transient current with temperature, field, time, electrode materials and sample thickness etc.

A lot of work on charge storage has been carried out on cellulose acetate [11–13] and polyvinyl acetate (PVAc) [14–17]. The physical processes leading to electret state of these polymers are clear. However, the effect of blending of these two on charge storage and transport mechanism is still not well understood. Polymer blends are heterogeneous mixtures and the possibility of charge trapping at the grain boundaries of the individual materials is higher in them. It has been shown that polyblend samples are better charge storer [18, 19]. Investigations concerning the dependence of electrical properties on structure are, however, presently very sparse.

In the present paper a polyblend consisting of cellulose acetate and polyvinyl acetate has been studied in detail in two weight proportion under different forming conditions. This particular combination in which the two components have the same functional groups, forms a thermodynamically compatible system [20].

## **2. Experimental details**

Isothermal immersion technique was utilized for preparing films of polyblends. Both the polymers cellulose acetate (CA) and polyvinyl acetate (PVAc), having average molecular weight 80,000 and 50,000 respectively were dissolved separately in dioxane. The two solutions, each of which, with a concentration of 100 g/L were then mixed in proportions of 90:10 and 75:25 by weight proportion of CA and PVAc, designated as  $A_1$  and  $A_2$  respectively. The solution was continuously stirred for half an hour by means of a teflon-coated magnetic stirrer. Thereafter, it was stirred and heated up to 313 K to yield a homogeneous and transparent solution. The glass beaker containing the solution was then immersed in a constant temperature oil bath. Ultrasonically, cleaned vacuum metallized microscopic glass slides were immersed vertically into the solution for about half an hour. The majority of measurements were made with aluminium electrodes except for a limited number of observations which are made on samples provided with copper, silver and lead electrodes. After the deposition of film, the glass slide was taken out and slowly dried in a saturated dioxane atmosphere. Films were further dried for 24 h in a dry atmosphere and were finally kept in an oven at 313 for 24 h to evaporate residual solvent. This was followed by room temperature outgassing at  $133.33 \times 10^{-5}$  N/m<sup>2</sup> for 24 h. Polyblend films of 20  $\mu$ m thickness were used unless otherwise stated. The thickness which was estimated [21] by measuring the capacitance of fabricated sandwiches taking the dielectric constant  $\epsilon$  of CA and PVAc as 3. The transient currents were measured in the discharge mode, as the charging current is a sum of the absorption current and the conduction

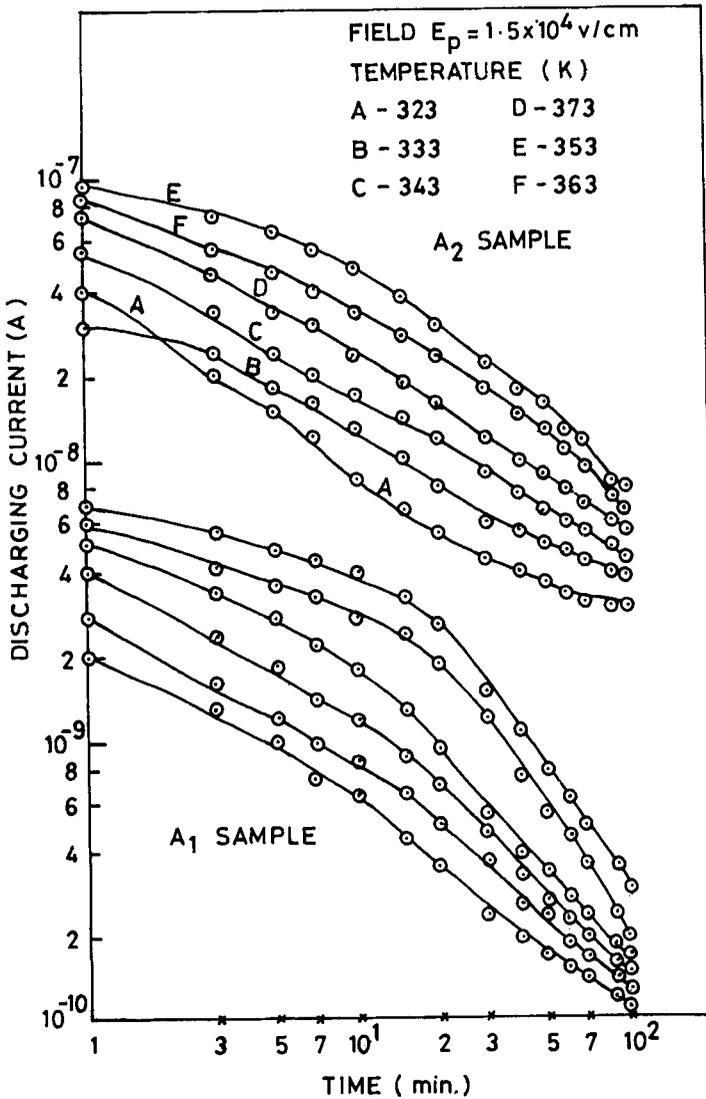
current. Different steps for the preparation of a thermoelectret are as follows (i) the sample is heated to the desired polarizing temperatures ( $T_p$ ); it is kept at  $T_p$  for some time (in the present case, 2 h) to reach thermal equilibrium; (iii) then, an electric field ( $E_p$ ) is applied at  $T_p$  and kept on for a period of polarizing time ( $t_p$ ); (iv) it is then cooled slowly under the field application, to room temperature. The field is then removed. The effect of field variation in current was recorded by increasing the voltage in steps of 10 V at fixed temperature, while temperature variation was recorded by keeping the field constant and increasing the temperature in steps of 10 K. In the present study, the samples were thermally polarized with fields of  $(1.5-4.5) \times 10^4$  V/cm at various temperatures (323–373 K) for  $10^2$  min during which the transient currents in discharging mode has been observed at suitable interval of time, after the removal of the field. The current was recorded, with a Keithley 600 B electrometer which was carefully shielded and grounded to avoid ground loops or extraneous electrical noise, as a function of applied field, temperature and charging time as reported earlier [15, 22].

### 3. Results and discussion

The time dependence of the discharging current in CA:PVAc blend samples with 90:10 and 75:25, weight % ratio of the two polymers over a time period of 1– $10^2$  min, in the temperature range 323–373 K with polarizing field  $1.5 \times 10^4$  V/cm are shown in figure 1. The observed discharging current has been found to be of the order of  $10^{-10}$ – $10^{-7}$  A. Figure 2 depicts such currents for samples  $A_1$  and  $A_2$  at 323 K with various polarizing fields  $(1.5-4.5) \times 10^4$  V/cm. As can be seen from figure 1, the magnitude of the discharge currents at a particular time show a marked dependence of temperature. The various plots have been found to be characterized with two regions; one short time region and the other long time region. The curves become steeper at longer times. The value of  $n$ , i.e. of slope for sample  $A_1$  and  $A_2$  become smaller ( $\approx 0.45$ ) in the shorter time region, as the time of discharge increases, while that for long time region an increase in the value of  $n$  almost approaching to 1.6 is found. There appears to be a process of thermal activation over the whole range of temperature. The observed time dependence of the current transients may be considered to follow Curie-von Schweidler law

$$I_a(t) = A(T)t^{-n} \quad (1)$$

where  $I_a$  is the absorption current,  $t$  the time and  $A(T)$  a temperature-dependence factor. The faster decay of current in long time region for different samples indicates the existence of energetically distributed localized traps in the sample. Trapping of charges can take place at various trapping sites—surface states, chain foldings and molecular disorder [12]. Small irregularities observed in some cases may be due to presence of charge domains inside the material [23]. The polyblend is a heterogeneous mixture and as such has a very large number of trapping sites. It seems that at lower charging temperatures only shallow traps are involved which get emptied at these temperatures. But as the temperature rises, more and more deeper traps are involved. The trapping of charge carriers (holes and electrons) in the deep trap levels may lead to induced dipole formation. The energy required for their disorientation and the release of charge carriers from these trapping sites will be high and as such the discharge current is small [24]. The bulk of the measurements of the transient currents



**Figure 1.** Current transient versus time curves at various temperatures (323, 333, 343, 353, 363 and 373 K) with constant poling field ( $1.5 \times 10^4$  V/cm) for  $A_1$  and  $A_2$  samples.

in blend sample were made with  $20 \mu\text{m}$  samples. A limited number of measurements, however, were made with samples of 10, 30 and  $40 \mu\text{m}$  thickness over a temperature range with aluminium, copper, silver and lead electrodes (results not shown). These results indicate that the transient current in blend of CA:PVAc may not be dependent on the electrode materials as well as thickness of the samples within the range of fields employed.

The discharge current measured at prescribed times (i.e. isochronals) plotted against temperature for two polyblend samples are shown in figure 3. These plots are characterized by well defined peak at 363 K. The observed broadness of the isochronal peaks may also have been due to overlapping of a number of relaxation mechanisms. The activation energy ( $E$ ) value obtained from plots (figure 4) of the discharge current

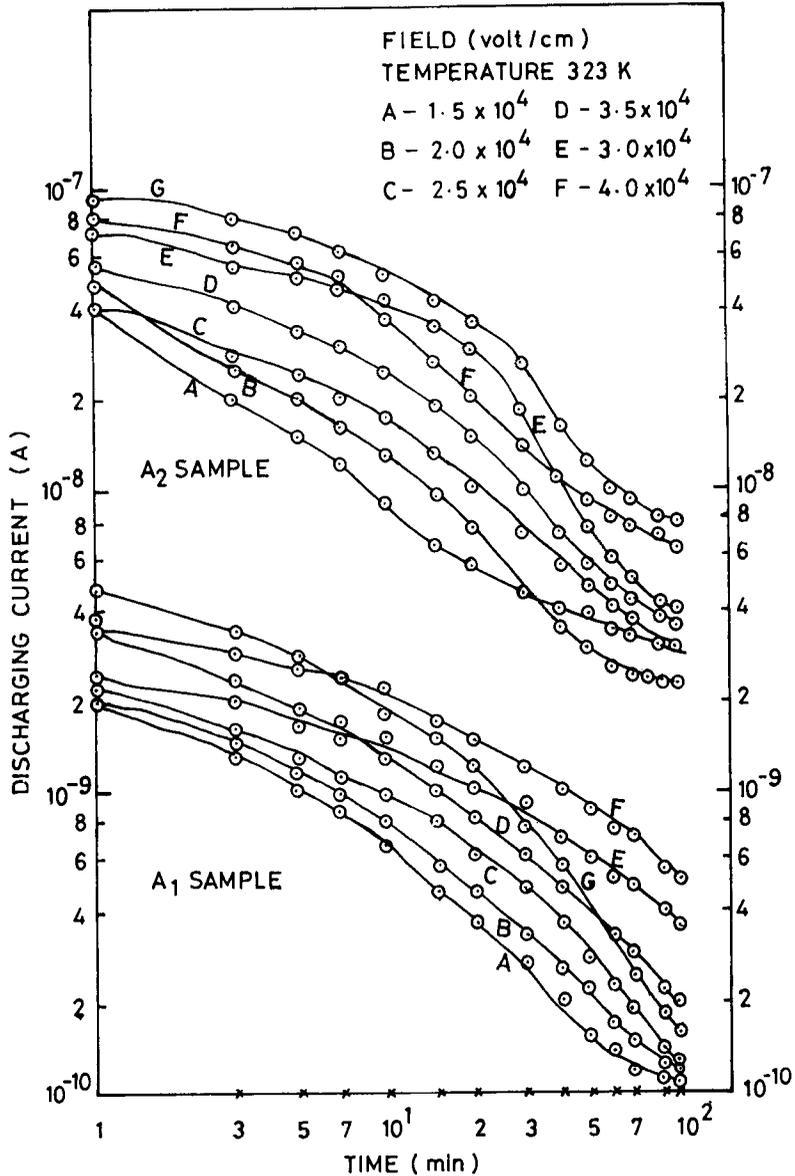


Figure 2. Current transient versus time curves with various poling fields ( $1.5 \times 10^4$ ,  $2.0 \times 10^4$ ,  $2.5 \times 10^4$ ,  $3.0 \times 10^4$ ,  $3.5 \times 10^4$ ,  $4.0 \times 10^4$  and  $4.5 \times 10^4$  V/cm) at 323 K, for  $A_1$  and  $A_2$  samples.

versus  $10^3/T$  at various prescribed times (1 min, 5 min, 10 min, 30 min, 70 min and 100 min) for various samples with different ratios of the polymers ( $A_1$  and  $A_2$ ) are found to vary from 0.61 to 1.21 eV. The value of  $E$  agrees well with what obtained from the TSDC results [25]. For samples with a fixed weight ratio of the two polymers, the activation energy value has been found to increase with increase in time of observation of the discharge current. Moreover, at any fixed time the activation energy value increases with increasing concentration of polymer. Increasing concentration of PVAc in the polymer matrix is considered to play an important

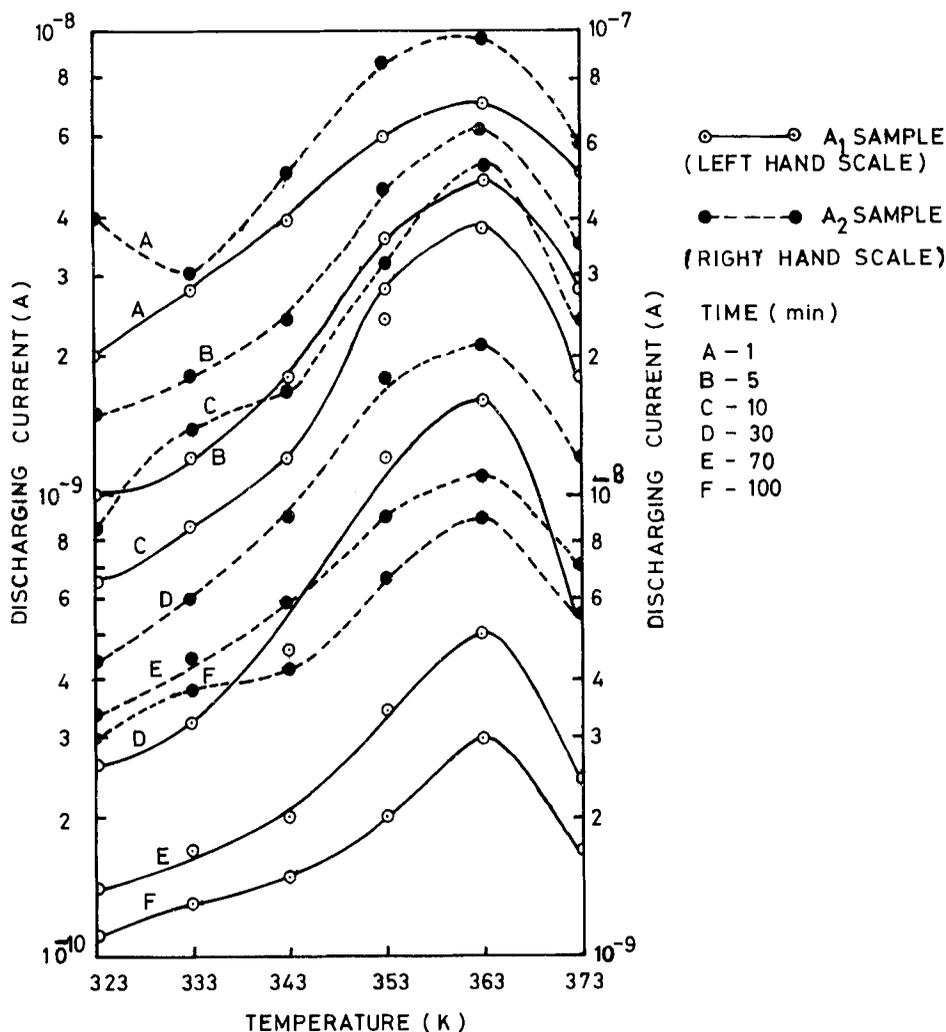


Figure 3. Current transient versus temperature curves at constant times (1 min, 5 min, 10 min, 30 min, 70 min and 100 min) for A<sub>1</sub> and A<sub>2</sub> samples.

role in modifying the trap structure in the sample causing more and more deeper traps, due to which the observed activation energy value is more.

In the segments, mobility may be increased after the complete phase transition and thus the possibility of injection of charge carriers near the electrodes and their drift seem to be possible by self motion of charge carriers/ions above the  $T_g$  range. Above  $T_g$  of the polymer a sudden change in its volume may occur and thus structural rearrangements of chains (segments) may be possible due to sufficient mobility of segments [26]. It is difficult to say about the contribution of individual homopolymer molecular orientations to this high temperature isochronal peak, since both CA and PVAc are partial polar polymer having  $T_g$  around 373 and 333 K respectively. However, the broadness of the peak may be explained by assuming a distributed or multiple dielectric relaxation may be due to distribution in activation energy when the rotation of the dipoles does not proceed in the same environment. Alternatively, it may be due to distribution in relaxation time, when the rotational masses of the

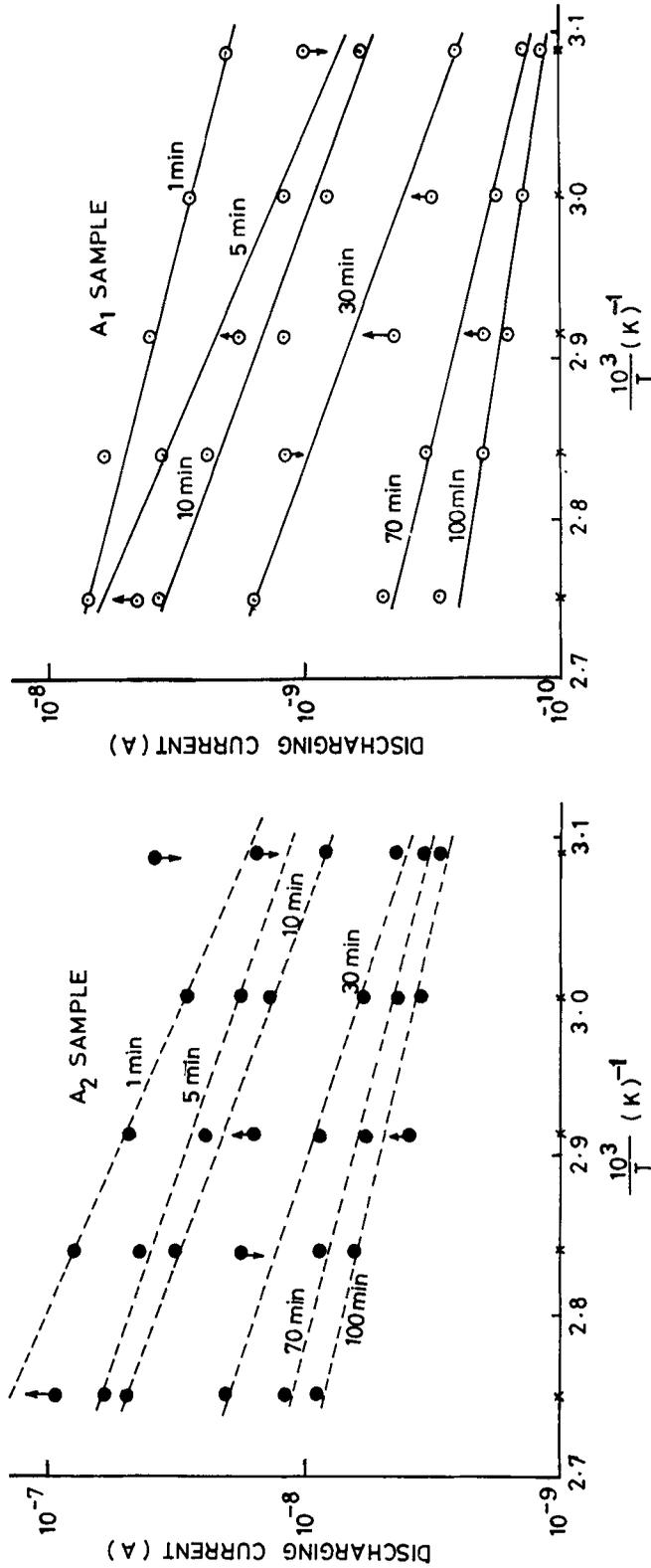


Figure 4. Current transient versus  $10^3/T$  curves at constant times (1 min, 5 min, 10 min, 30 min, 70 min and 100 min) for  $A_1$  and  $A_2$  samples.

dipoles are not equal. The broadness of the peak in the present case is, however, most likely to be distribution in relaxation time, because the peak is occurring near  $T_g$  of the two polymer, where the side groups move in unison with the main chain, differing in masses [27, 28]. Because the distribution of dipoles in the amorphous phase is most likely to be random, it is expected therefore, this complex process involving both the distribution of the activation energy and relaxation time.

As temperature increases mobility of carriers also increases, hence all the deeper traps are filled. Release of a large number of charge carriers from the traps during the process may then result in high return rate of carriers leading to blocking of electrodes causing a decrease in current. The charge injection from electrodes with subsequent trapping of injected charges in near surface region giving rise to homospace charge and the thermal release of charge carriers from the traps. Before the trapped space charge injected at higher fields, is thermally released, a space charge barrier is presented to the electrode which suppresses the entrance of charge carriers into the sample. Thus, the observed current remains smaller than its corresponding value.

Addition of PVAc in CA produces heterogeneous structure and plasticization effect [19]. Because of the heterogeneous structure, charge carriers injected in the bulk may pile at the phase boundaries. Plasticization causes loosening of the structure and greater mobility of charge carriers resulting in the increase of current. In CA:PVAc matrices containing different percentage at least two phases coexist and discontinuity of structure at such boundary increases. Because of the carrier conductivity in different phases, the carriers get trapped at the interphases of phase boundary. Further, the dipoles may also originate due to trapping of both positive and negative charge carriers in the deep traps in such a way as to form induced dipoles. Such trapped charge carriers may be generated in the bulk from the impurities thus they lead to induced dipole polarization in the polyblend films [12]. It is also possible that contribution of a permanent dipole of the host material is masked due to induced dipoles. In the blends, dipoles of the polar compound are so constrained that under the field, they either do not orient or their contribution to the total polarization is almost negligible as compared to the contribution of induced dipoles, which are formed in the bulk by the deep trapping of charge carriers originating in the bulk. The large value of activation energy may be taken as an indication of induced dipole formation because in this case the energy required to disorient them and subsequently release charge carriers from the trapping sites is expected to be higher [18, 19].

The Curie-von Schweidler type of time dependence has been observed for many polymers with the index “ $n$ ” close to unity. A number of mechanisms may be invoked to explain such time dependence. It is therefore, not possible to specify the origin of transient currents in blend from analysis of time dependence alone. The polyblend samples used in the present case are expected to possess various dipoles due to the presence of PVAc. Polyvinyl acetate (PVAc) contains polar group C=O in its main chain having a weak permanent dipole moment. The structure of cellulose acetate with a polar main chain with polar side groups enhances formation of the carriers, which accumulate at the electrode during formation. These polar groups form permanent dipoles which can be oriented during the polarization process. These considerations suggest that it is reasonable to ascribe the observed discharge current due to the dipolar mechanism. However, the experimental facts in the present case are not consistent with the behaviour of discharging current. In the case of dipolar mechanism, the discharging current should vary linearly with the field intensity.

However, in the present case, the discharging current depends on field at random manner (figure 2). It was, therefore, unlikely that the dipolar orientation involving the relaxation process was responsible for the isochronal current peak observed at the high temperature range in this work. On the other hand, the observed values of “*n*” for shorter and longer times as well as the thermal activation of discharging currents at various fixed times counted after the removal of the charging field indicate that the space charge due to accumulation of charge carriers near the electrodes and trapping in the bulk may also be supposed to account for the observed current. In the case of transients governed by space charge, the peak in the current time curve should occur at a time

$$t_m = \frac{0.786a^2}{\mu V}$$

where *V* is the applied voltage, *a* is the sample thickness and  $\mu$  the carrier mobility. To have a rough estimate of the time at which this peak should occur we used the values of *a*, *V* and  $\mu$  to be 20  $\mu\text{m}$ ,  $2.0 \times 10^4 \text{ V/cm}$  and  $10^{-11} \text{ cm}^2/\text{V}$ . It was found that  $t_m$  should approximately be equal to  $1.57 \times 10^3 \text{ s}$ . Thus, there is possibility of space charge relaxation occurring at sufficiently longer times. This may be due to trapping of charge carriers in sufficiently deeper traps. The observed temperature dependence (i.e. thermal activation) and the absence of any significant effects (i) electrode materials and (ii) sample thickness, makes tunneling unlikely as a possible mechanism to explain the nature of transient currents. The process of electrode polarization is also unlikely because of the absence of electrode effects and also because the observed “*n*” values are significantly different from the theoretically predicted model. The polymer films are known to be a mixture of amorphous and crystalline regions. The presence of localized states may lead to the localization of injected charge carriers giving rise to the accumulation of trapped space charge. The hopping mechanism, such as the one described by Lewis [29] required the existence of localized carrier trapping states, which had a distribution of energies. The observed time-dependence of the transient current would not be incompatible of such a process.

Struik [30] showed that solids like polymers are not in thermodynamic equilibrium at temperatures below their glass transition. For such materials, free volume enthalpy and entropy are greater than those they would be in the equilibrium state. The gradual approach to equilibrium affects many properties for example, free volume of the polymer may be decreased. The decrease in free volume lowers the mobility of chain segments and also charge carriers such as ions. This decrease in mobility may be expected to reduce dc conductivity. At higher electric fields, the changes in mobility may take place faster than at lower fields and also recombination of charge carriers may be more.

#### **4. Conclusion**

Considering the effects of charging field, temperature and time on the transient current in CA:PVAc blend, we conclude that the polarization in blend is due to trapping of the bulk charges, produced charges as well as the electrode injected charges in the deeper traps and their subsequent alignment due to step field.

## References

- [1] R M Hill, *J. Phys.* **D8**, 2488 (1975)
- [2] D K Davies, *J. Phys.* **D2**, 149 (1969)
- [3] A K Jonscher, *J. Phys.* **D11**, 601 (1978)
- [4] H J Wintle, *J. Non. Cryst. Solids* **15**, 471 (1974)
- [5] D K Dasgupta and K Joyner, *J. Phys.* **D9**, 829 (1976)
- [6] S Nakamura, G Sawa and M Ieda, *Jpn. J. Appl. Phys.* **18**, 995 (1979)
- [7] H J Wintle, *IEEE Trans Electr. Insul.* **EJ-12**, 97 (1977)
- [8] B V Hamon, *Proc. Inst. Electr. Eng. London Monographs* **27**, (1952)
- [9] R H Petridge, *Polym. Lett.* **5**, 205 (1967)
- [10] A Servini and A K Jonscher, *Thin Solid Films* **3**, 341 (1969)
- [11] A Kumar and R Nath, *Phys. Status Solidi* **A61**, 301 (1980)
- [12] P K C Pillai, G K Narula, A K Tripathi and R G Mendiratta, *Phys. Status Solidi* **A67**, 649 (1981)
- [13] P K Khare, *Indian J. Pure Appl. Phys.* **32**, 160 (1994)
- [14] P K Khare, J M Keller and S C Datt, *Indian. J. Pure Appl. Phys.* **29**, 714 (1991)
- [15] P K Khare, M S Gaur, Alka Bajpai, R K Pandey and A P Srivastava, *Indian J. Pure Appl. Phys.* **31**, 326 (1993)
- [16] P C Mahendru, K Jain, V K Chopra and P Mahendru, *J. Phys.* **D8**, 305 (1975)
- [17] P C Mahendru, K Jain and Praveen Mahendru, *J. Phys.* **D11**, 1431 (1978)
- [18] P K Khare and A P Srivastava, *Indian J. Pure Appl. Phys.* **30**, 102 (1992)
- [19] P K Khare, M S Gaur and A P Srivastava, *Indian J. Pure Appl. Phys.* **31**, 102 (1993)
- [20] C Yasile, S Ioan, N Asandei and I A Schneide, *Macromol. Chem.* **6**, 24 (1969)
- [21] P K Khare, M S Gaur and A P Srivastava, *Indian J. Pure Appl. Phys.* **32**, 14 (1994)
- [22] P K Khare and Ranjeet Singh, *Polymer International* **34**, 407 (1994)
- [23] M R Bhide and S Rao, *Pramana – J. Phys.* **4**, 271 (1975)
- [24] P K C Pillai, G K Narula, A K Tripathi and R G Mendiratta, *Phys. Status Solidi* **A77**, 693 (1983)
- [25] P K Khare, Thesis Ph.D., Study of thermostimulated discharge currents of doped films in organic systems Saugor (MP) India (1989)
- [26] P K Khare and R S Chandok, *Polymer International* **35**, (1994)
- [27] J Van Turnhout, *Thermally stimulated discharge of polymer electrets* (Elsevier, Amsterdam, 1975), pp. 106–130
- [28] Van J derschueren, *J. Polym. Sci. Polym. Phys. (USA)*, **15**, 873 (1977)
- [29] T J Lewis, *Conf. on Electr. properties of organic solids*, (Inst Phys. Chem. Wroclaw Tech Univ Poland Ser No. 7, Conf No. 1, pp. 146–62
- [30] L C E Struik, *Physical aging in amorphous polymers and other materials* (Elsevier, Amsterdam, 1978)