Drift mobility determination using surface-charge decay technique in polyvinylidene fluoride (PVF_2)

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Drift mobility of charge carriers in pure and iodine doped PVF_2, has been determined by surface-potential decay method. The mobility $\sim 8\times 10^{-11}$ cm^2 V^{-1} s^{-1} and $\sim 10^{-8}$ cm^2 V^{-1} s^{-1} have been encountered in pure and iodine doped PVF_2 respectively. The increase in mobility with doping is attributed to the charge transfer complex formation. The existence of charge transfer complex is found from the analysis of u.v. and visible spectra of doped samples. It is concluded that charge carrier conduction in PVF_2 may be due to a hopping process.

INTRODUCTION

In recent years there has been an increasing interest in the conduction mechanism of poly(vinylidene fluoride) (PVF_2). This interest is a consequence of the many useful applications of PVF_2 in electronic engineering as dielectrics[1,2] pyro- and piezo-electrics[3-5] and infra-red detectors[6] etc. At room temperature PVF_2 exists in two crystalline[7,8] forms, α and β. Thd α form with monoclinic molecular arrangement has the paired dipoles directed to molecular axes; whereas, in the β form with rhombic molecular arrangement, the large dipoles are directed normally to the molecular axes. The solvent-cast PVF_2 film in which β crystals are preferentially oriented are investigated in the present work.

Conduction mechanisms in polymers can be well understood in terms of carrier mobility and other transport parameters. Carrier mobility encountered in polymers generally lie in the range of 10^{-4}–10^{-11} cm^2 v^{-1} s^{-1}. Several special techniques viz., photo Hall effect[9], time of flight method employing pulsed light[10] and electron beam[11], surface charge decay[12] and zerographic discharge[13], have been used for the determination of mobility.

It has been reported by previous workers[14] that the carrier mobility can be greatly increased by doping the polymer with iodine. Iodine enters the polymer as a neutral molecule and some of which form charge exchange complex with the polymer. A charge transfer complex means the interaction between two species, the strength of which lies between a full chemical bond and a small orbital overlap.

Here, the carrier mobility in PVF_2 and its charge transfer complex with iodine is determined from the surface potential decay technique. The results of the investigations are discussed in view of understanding the conduction mechanism in PVF_2.

EXPERIMENTAL

Poly(vinylidene fluoride) (PVF_2) was supplied by Polysciences Inc. U.S.A. The films used in experiments contained predominantly β-form crystals (henceforth called β-form films). Films of pure PVF_2 were made by casting a dimethyl sulphoxide solution of PVF_2 onto a clean glass plate at 60°C. Due to poor adhesion of PVF_2 with glass, the film was detached and cut into a convenient size for the experimental investigations. A film thickness of ~ 150 micron was obtained. The different samples of I_2 doped PVF_2 were prepared by dissolving the known quantities of I_2 by weight of PVF_2.

For surface potential decay measurements, the sample was charged at the open surface, with lower electrode grounded, with the help of a corona unit kept at a fixed distance over the sample. The charging process continued for 30 s. The subsequent decay of the surface potential was measured with a vibrating probe, specially developed for this purpose. All the measurements were made at room temperature.

The optical absorption spectra of pure and iodine-doped PVF_2 were taken in both the u.v. and visible ranges.

RESULTS AND DISCUSSION

The surface potential decay characteristics observed for pure and iodine doped PVF_2 samples are shown in *Figure 1*. The inset of *Figure 1* gives the plot of the initial surface potential V_0 *versus* percentage of iodine content in PVF_2: I_2 complex. The V_0 first decreases with increase in the iodine content and then increases again after going through a minimum. This shows that the charge acceptance property of iodine-doped PVF_2 is poor in 10 to 20% range of iodine content.

The carrier mobility for all the samples is calculated from the surface potential decay characteristics given in *Figure 1*, using the Berger and Lanyon's formula[15]:

$$\mu=\left(\frac{V_0}{V_t}-1\right)d^2/2V_0t \qquad (1)$$

where V_t is the surface potential at time t and d is the thickness of the sample. The calculated values of mobility

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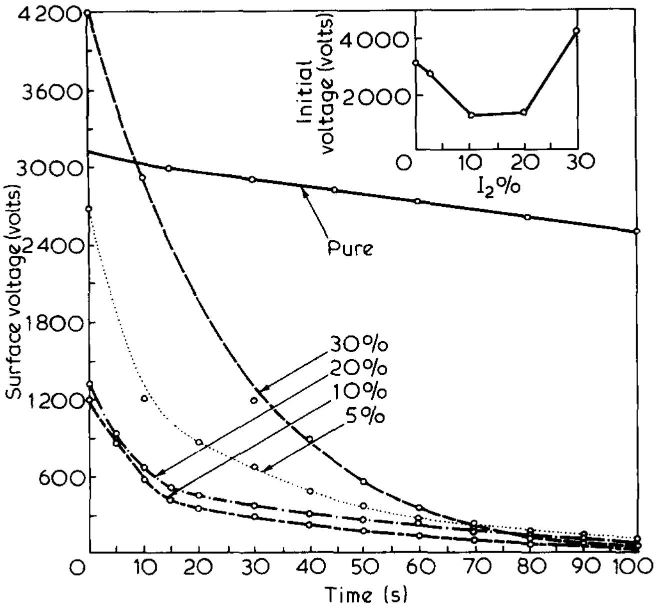

Figure 1 Surface-potential decay characteristics of pure and iodine doped PVDF. Inset: Plot of initial voltage vs. percentage iodine content by weight

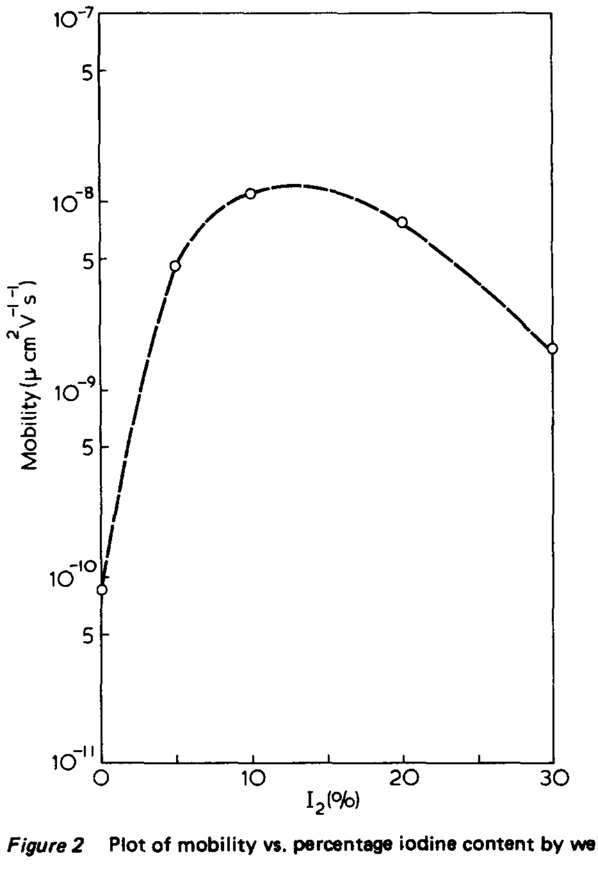

Figure 2 Plot of mobility vs. percentage iodine content by weight

are plotted as a function of the iodine content as shown in *Figure 2*. It can be seen that the mobility value increases with I_2 content and is maximum at 10% iodine content. A similar type of behaviour has been observed experimentally by previous workers[16] in conductivity studies of organic charge transfer complexes with dopant concentration. No suitable explanation is available to explain the maximum in the plots as observed in *Figure 2*. However, the increase in mobility by doping the polymer can be interpreted in terms of the charge transfer complex formation as done by Davies and others[14,17]. The formation of charge transfer complex in polymers could be verified by examining the u.v. and visible spectra of the doped polymer. *Figure 3* shows the typical optical absorption of pure and iodine doped PVF_2 (5% I_2) in u.v. and visible ranges. The band centred around 280 nm can be interpreted as the formation of charge transfer complex between iodine and PVF_2.

It has been shown[18] that a variety of trapping centres exist in polymers and the charge carriers are predominantly located in these trapping centres. The charge transfer complex formation effectively reduces the trapping effects. And, as the mobility in polymers being trap-modulated, charge transfer complex formation results in the increase of mobility. It is known, from previous studies[3,13] on pyroelectric phenomenon in PVF_2, that this phenomenon is due to the trapped space charge embedded in the film. This implies that the trapping of charge carriers should affect the conduction processes and transport parameters in PVF_2. The increase in the carrier mobility with iodine doping gives that trapping effects are greatly reduced in PVF_2. Whether iodine doping of PVF_2 really affects the embedded trapped space charge, can be revealed from the pyroelectric studies of PVF_2:I_2 films. The work on this problem will be published in near future. From the location of charge carriers in traps and the extremely low value of mobility $\sim 8 \times 10^{-11}$ cm² v^{-1} s^{-1} in PVF_2 it can be concluded[20,21] that the conduction process could be described by hopping model. The hopping model involves localized states, where carrier jump from one state to another.

CONCLUSIONS

The following conclusions can be drawn from the present studies:

(i) The increase in carrier mobility in iodine doped PVF_2 films is found and is explained on the basis of charge transfer complex formation.

(ii) The mobility value $\sim 10^{-8}$ cm² v^{-1} s^{-1} is found to be maximum at 10% I_2 content in PVF_2:I_2 samples.

(iii) The conduction process in PVF_2 is attributed to the hopping of charge carriers in the localized states.

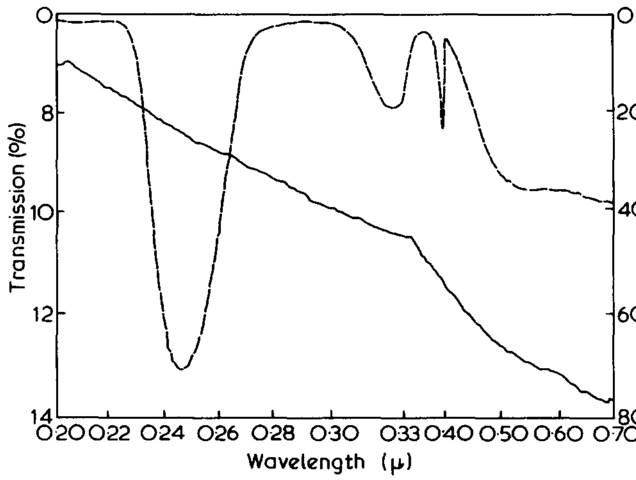

Figure 3 Transmission spectra of pure (——) and iodine doped PVDF (– – –) in visible and u.v. range

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