CHAPTER VI

BREAKDOWN STUDIES

6.1 Introduction

Thin films are widely used in passive devices, field effect transistors and microelectronic circuits. In all these applications the stability of the film is an important factor. Hence the study of the electrical breakdown properties of thin films is essential. These investigations play an important role in the systematic development of devices [1]. Breakdown studies can be carried out on thin films because the experimental voltages are low, testing can be repeated many times on a single sample with non-shorting breakdown and observations are not disturbed by gas discharge [2].

In the different theories proposed upto now, a crucial point is observed to establish whether the breakdown results from a local event or rather is the consequence of a phenomenon propagating with an increase of intensity. Experiments have been performed on samples subjected to pulses of breakdown voltage [3] or on samples biased in the pre-breakdown region and illuminated by flashes of light [4] or through investigations of pre-breakdown light emission [5]. Many experiments on films have shown the dependence of the dielectric strength upon the film thickness and temperature [6]. Extensive work has been done on the breakdown

properties of insulating polymers [7-17]. The criterion that determines breakdown is a form of self- healing [7,14] However, no work has been done on thickness as well as temperature dependence of breakdown properties of different conducting polymer films.

This chapter deals with the breakdown studies on polyaniline-EB, lightly doped polyaniline and polypyrrole, and polypyrrole/polyaniline-EB blend films prepared by film casting technique.

6.2. Theory

Many theories have been suggested by various researchers to explain the different types of breakdown mechanisms in inorganic solids and semiconductors. Since the polymers of the present study, behave like semiconductors, these theories may be extended to explain the breakdown in these film also. In this section the breakdown theories proposed by Forlani and Minnaja, O'Dwyer and Klein and Gafni have been discussed.

6.2.1 Theory of Forlani and Minnaja

This theory describes the onset of breakdown in an ionic crystal by considering the injected electrons from the cathode as free electrons in the conduction band of the sandwitched material. The acceleration of these electrons are impeded by electron-phonon collisions. Electrons with energy larger than the unstable equilibrium energy, gain energy from the

applied field till they attain the ionization energy of the dielectric crystals. The current is then enhanced by the creation of additional carriers by ionization collisions. The critical conditions for breakdown is the film thickness. The thickness dependence of the breakdown field strength (F_b) is obtained from the electron current equating the negative exponent of the avalanche multiplication factor, when the latter is evaluated at the film thickness 'd'. The expression given by Forlani and Minnaja [18] for the breakdown field is,

$$F_b = A\, d^{-\alpha}$$

where A is a constant. When log F_b is plotted against log d, a straight line with negative slope is obtained and the slope yields the value of α. Forlani and Minnaja have predicted that the value of α lies between 0.5 and 0.25. The above expression is based on the theory of electron phonon interaction [18]. Theories based on electron-phonon scattering state that the dielectric strength increases as the temperature is increased provided that the electron scattering is properly taken into account.

6.2.2. Theory of O'Dwyer

O'Dwyer theory incorporates a condition of current continuity during avalanche process which causes the field to be heterogeneous, being considerably larger at the cathode than elsewhere. The breakdown mechanism is associated with impact ionization. The instability is due to the positive feed back between the holes which are trapped by

impact ionization and the electrons which are injected from the cathode. The injection is enhanced by trapped holes owing to the increase in field at the cathode. This results in an increase in impact ionization and hole trapping. When this rise cannot be balanced by hole drift, breakdown occurs.

6.2.3. Klein's Theory

Klein and Gafni proposed the theory based on a succession of electron avalanche processes due to impact ionization and the injection of electrons into the conduction band when an electric field is applied across the thin film capacitor. An electron produced at the cathode causes an avalanche of free electrons by impact ionization and the positive charges are left behind in the insulator. These positive charges have a very low mobility and hence drift slowly to the cathode forming a positive charge cluster. This results in the enhancement of field at the cathode. The local injection rate of electrons increases and a finite probability is reached for an electron to hit the tiny charge cluster during transit through the insulator. The average cathode field during the transit of the charge cluster increases with film thickness. Hence the formation of large avalanche also depends on the film thickness, in addition to other parameters involved.

The breakdown, according to this theory, follows in a sequence of stages. In the initial sequence of stages, the whole of the specimen, causing the temperature to rise significantly. This enhances the critical conductivity leading to a thermally unstable state at the breakdown spot in the specimen

which finally results in voltage collapse through current runaway. Impact ionization may stop during voltage collapse, but the breakdown event continues until destruction occurs because of the thermally unstable state due to the temperature rise at the site. Thus a complete breakdown event comprises of, the initiation of breakdown, instability due to heating and finally destruction of the capacitor with voltage collapse.

6.3 Measurements

Thin polymer film capacitors with materials like polyaniline-EB, lightly doped polyaniline and polypyrrole, and polypyrrole/polyaniline-EB as the intermediate layer in the MPM sanswich structures have been fabricated as described in previous chapters. During breakdown, destruction of the polymer occurs by vaporization rather than by melting. Hence for the occurrence of non-shorting breakdown of the condenser one of the electrodes was deposited with low thickness.

6.4. Results and Discussion

Fig. 6.1(a to d) shows the doubly logarithmic plot of self healing breakdown field against film thickness for solution casted polymer films of the present study. The breakdown field strength is observed to vary from 4.5×10^4 to 8×10^8 V/m, 3.1×10^3 to 6.2×10^6 V/m, 1×10^4 to 5.2×10^5 V/m, and 4×10^3 to 5×10^5 V/m for Pani-EB, acid doped Pani, PPY and PPY/Pani-EB films respectively. The values of slope are found to

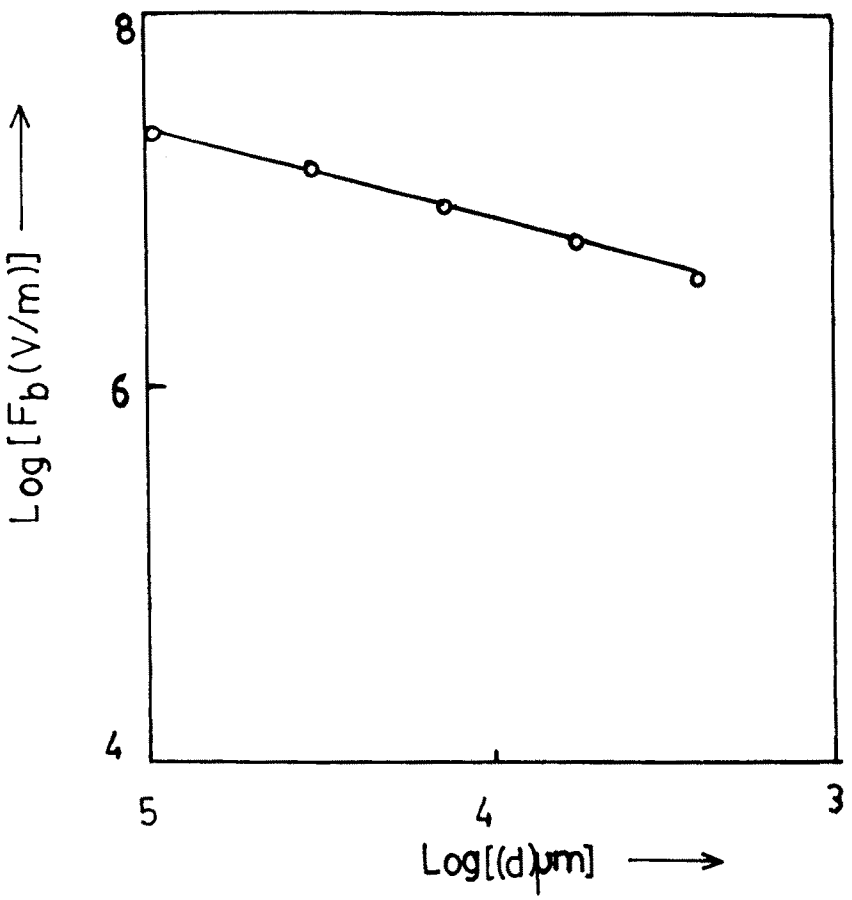


Fig. 6.1(a) Double logarithmic plot of self healing break down field against film thickness of Pani-EB film (d = 5μm)

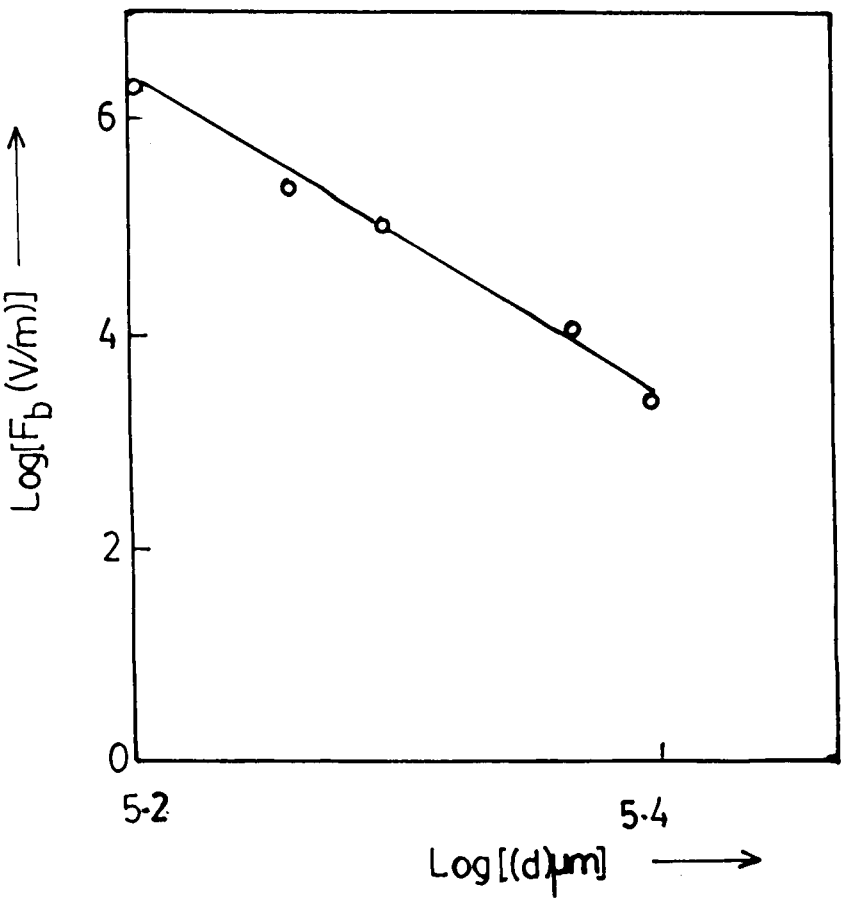


Fig. 6.1(b) Double logarithmic plot of self healing break down field against film thickness of acid doped Pani film(d = 4μm)

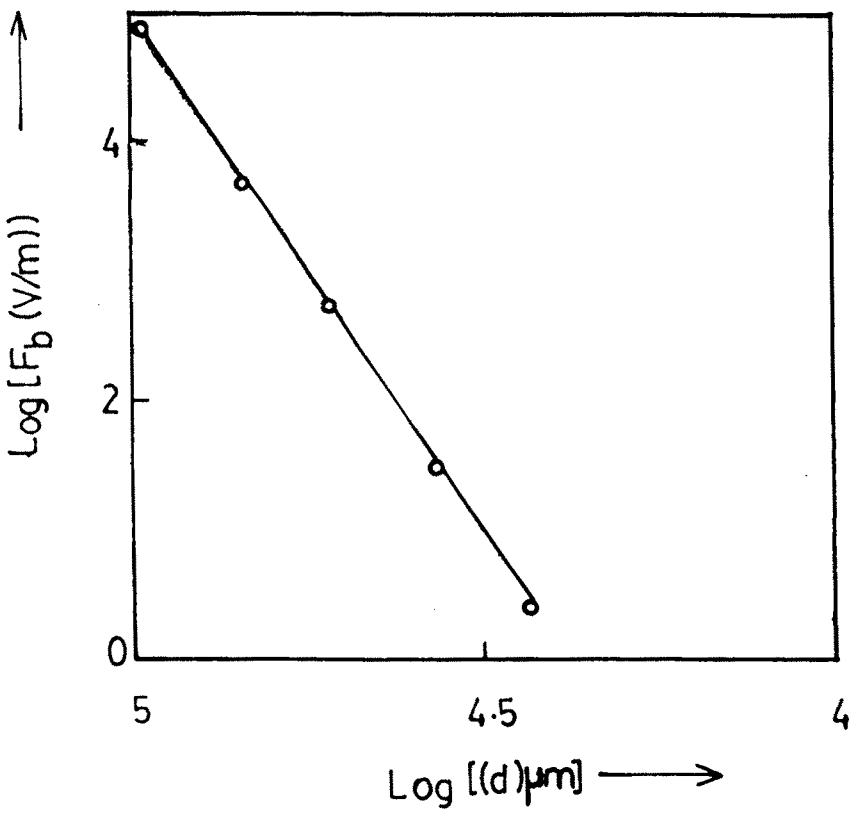


Fig. 6.1(c) Double logarithmic plot of self healing break down field against film thickness of PPY film(d = 6μm)

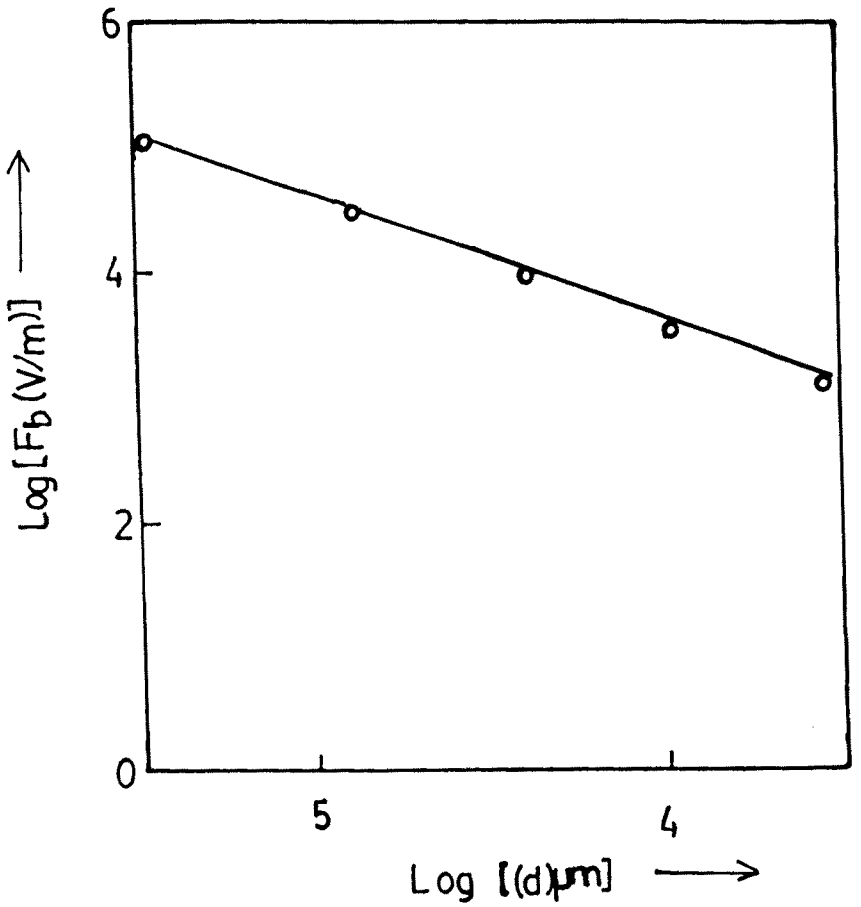


Fig. 6.1(d) Double logarithmic plot of self healing break down field against film thickness of PPY/Pani-EB blend film(d = 6μm)

be 0.48, 0.25, 0.26, and 0.49 respectively at room temperature for the above said films.

The observed breakdown field strength is of the same order as that obtained by earlier workers on thin polymer films and other dielectric materials [7,11,19-28]. The thickness dependence observed in these films can be explained based on the existing theories. Theories based on the impact ionization predicts a breakdown field independent of film thickness. Hence these theories cannot be applied here. Forlani - Minnaja theory [29,18] however agrees with the observed results. As mentioned in section 6.2, this theory predicts a thickness dependence of the form $F_b \propto d^{-\alpha}$ where α varies from 0.25 to 0.5. This theory also predicts that the higher value of α holds good for higher energy gap materials. In the present investigation, the values obtained being close to 0.5, the thickness dependence of the breakdown field in the Pani-EB, acid doped Pani, PPY and PPY/Pani-EB films obey the Forlani-Minnaja theory. The electrons injected into the conduction band of the material cause ionization. The current density increases rapidly with the applied field at some critical field where the self healing of electrons occurs. This grows as a cone with its maximum cross-section towards the anode. The Joule's heat produced by electron avalanche of breakdown field has been observed and reported by earlier workers on thin films of polymer materials like polystyrene [7,11], polyimide [14] and other dielectric materials. But in the case doped films the field strength values are low when compared to pure films.

Light emission is observed during dielectric breakdown measurements in the open atmosphere. This may be attributed to the recombination of carriers produced by impact ionization, indicating that breakdown starts by avalanching. Using a multimeter, the discontinuity in the top electrode and the continuity in the bottom electrode have been observed.

6.4.1. Temperature dependence of onset breakdown field

Fig. 6.2 (a-d) represents the variation of self healing breakdown field with temperature (303-383 K) for solution casted Pani-EB, acid doped Pani, PPY and PPY/Pani-EB films of typical thicknesses 5, 4, 6 and 2 μm respectively. From the figures it is observed that, the breakdown field for Pani-EB and acid Pani-EB films, almost constant upto a certain temperature (340 K) , after which it decreases suddenly with further rise of temperature. Similar sets of results have been observed for PPY and PPY/Pani-EB [Figs.6.2(c & d)] films.

A number of theories have been proposed to explain the temperature dependence of breakdown field. According to the theory of O' Dwyer electrons are assumed to be distributed over numerous energy levels in the valence band gap and a few electrons are in the conduction band due to thermal excitation. When these electrons have subjected to the applied field they gain energy and due to their finite life time, then fall into the shallow traps very near to the conduction band. According to this theory, the breakdown field should show a strong temperature dependence at all

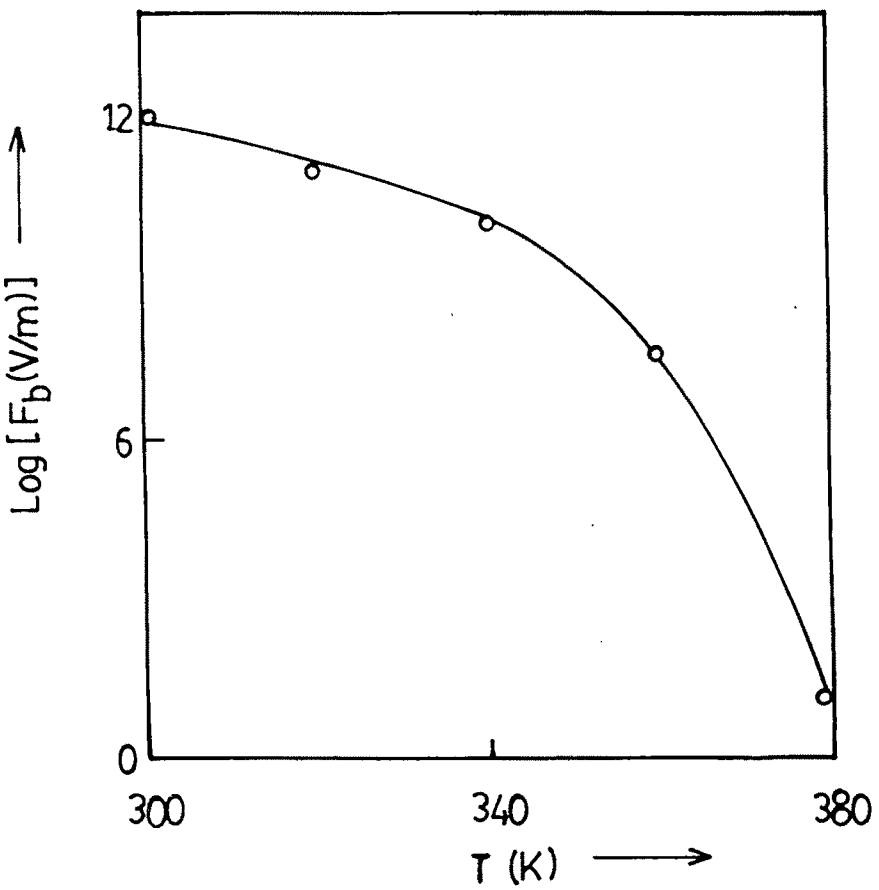


Fig. 6.2(a) Variation of self healing breakdown field (F_b) with temperature of Pani-EB film

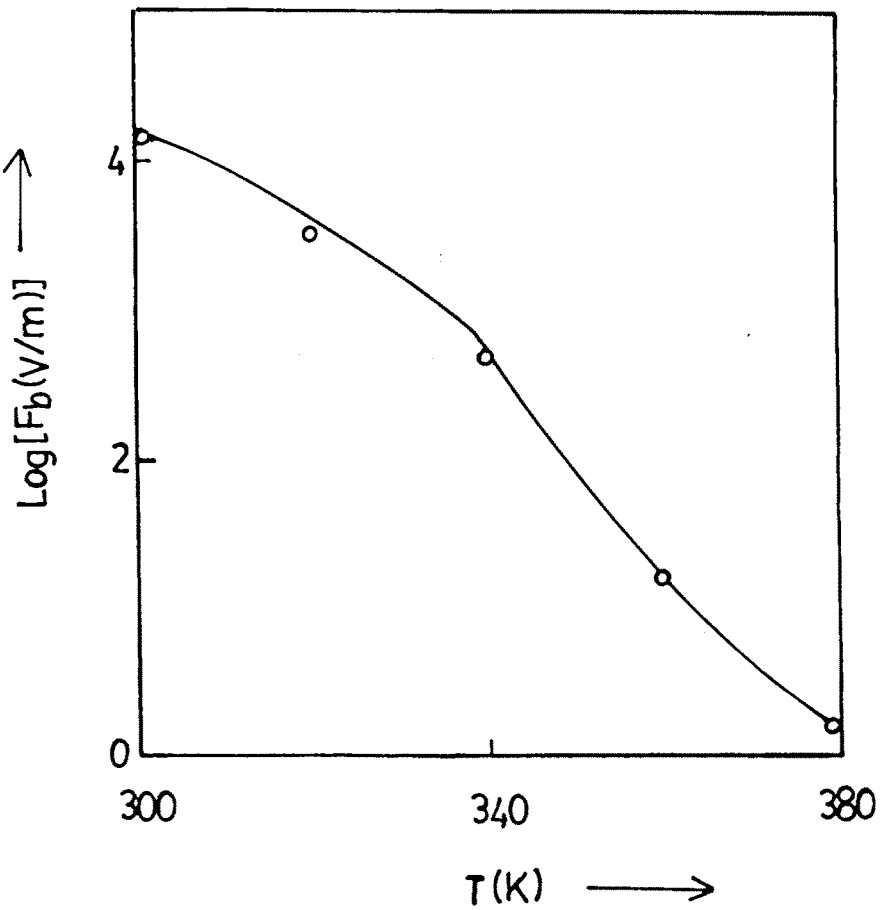


Fig. 6.2(b) Variation of self healing breakdown field (F_b) with temperature of acid doped Pani film

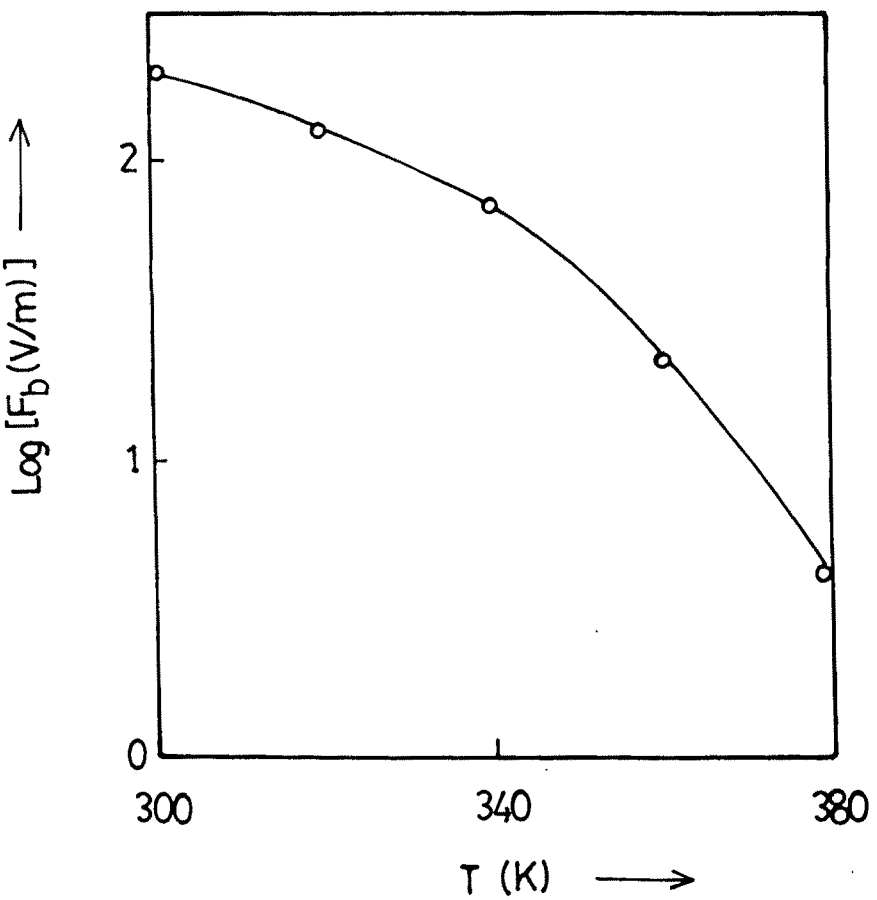


Fig. 6.2(c) Variation of self healing breakdown field (F_b) with temperature of PPY film

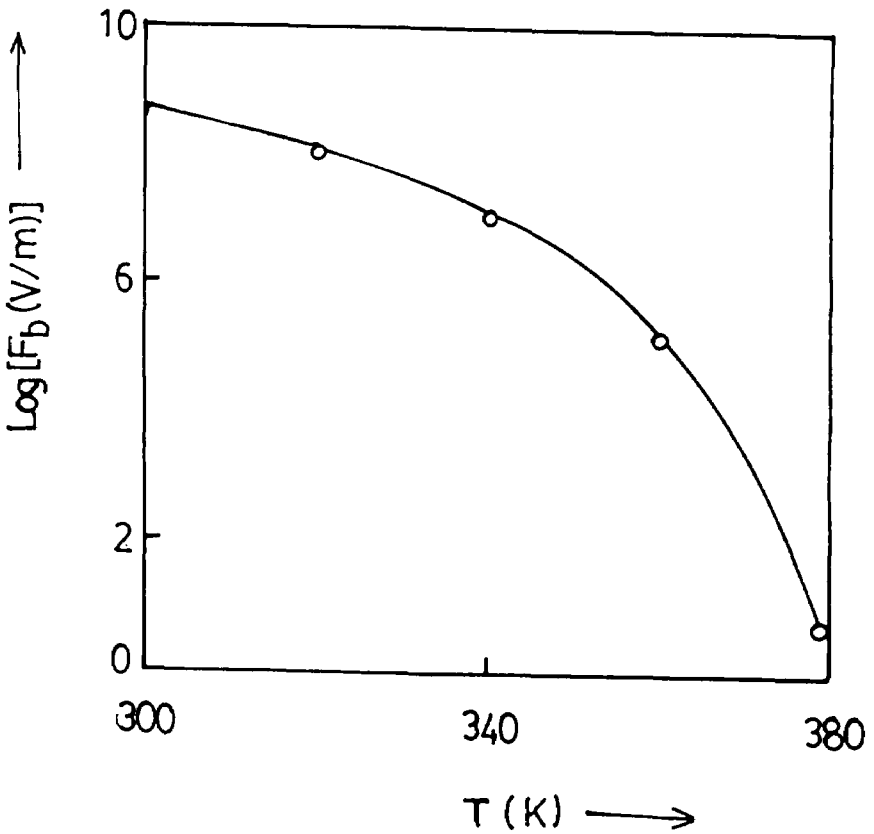


Fig. 6.2(d) Variation of self healing breakdown field (F_b) with temperature of PPY/Pani-EB blend film

temperatures. However, in the present study, the temperature dependence has been observed only after a certain temperature, viz., 340 K for both Pani-EB and PPY/Pani-EB films. Hence this theory is inadequate to explain the observed behaviour. According to the intrinsic breakdown theory, the breakdown field strength should increase with temperature, i.e., the slope of the breakdown field versus temperature curve should be positive. But the observed experimental slope is negative. Therefore the intrinsic breakdown field theory cannot be applied to explain the temperature dependence of Pani-EB and PPY/Pani-EB films.

Forlani and Minnaja's field emission theory [29] suggests that at lower temperature the breakdown occurs by an avalanche initiated by tunnel emission of electrons at the cathode into the conduction band of the dielectric. Hence at lower temperatures, the breakdown field is independent of temperature. This concept explains the experimental observation in which the breakdown field remains constant upto 340 K for both the films. At high temperatures, the electron injection is governed mainly by Schottky emission [18] rather than tunnel effect. As a consequence, the breakdown field strength decreases with increase of temperature, provided the electron-electron collision is taken into account. Due to dominant roles of the electron image force on the shape of the potential barrier, the decrease of breakdown field with the increase of temperature can be explained by the relation

$$F_b = \phi_{eff} E/kTqd$$

where ϕ_{eff} is the effective height of the potential barrier at the metal-insulator interface and E is the difference between the mean energy of the electrons required to ionize the dielectric and the mean energy of the emitted electrons. A decrease in the breakdown voltage can occur due to the lowering of bonding strength with increase of temperature. The breakdown voltage values of the doped samples are low as compared to that of pure samples. A sudden decrease is observed in the breakdown field (F_b) of both the films above the temperature 340 K. This is due to deformation of the polymer materials above the glass transition temperature T_g.

6.4.2. Breakdown patterns

Breakdown patterns have been classified into three types, viz.,

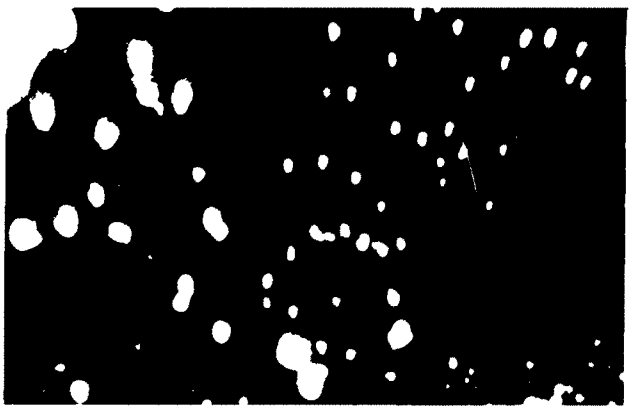
i. Single hole

ii. Propagating and

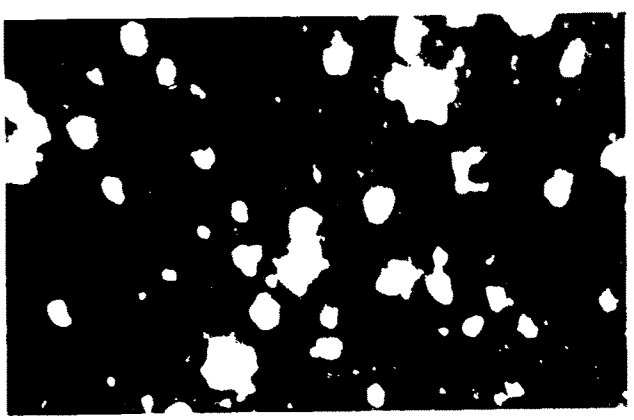
iii. Maximum

by Klein and Burstein [30] after their studies on SiO capacitors. The first two kinds are attributed to the localized flaws in the dielectric destroying a small area (single hole) or a large area (propagating) of the dielectric. The third one is regarded as characteristic of the ultimate breakdown strength of the film material.

The breakdown patterns of casting Pani-EB, acid doped Pani, PPY and PPY/Pani-EB films observed under transmitted light are shown in Figs. 6.3 (a-d). These figures show the single hole patterns for Pani-EB, acid

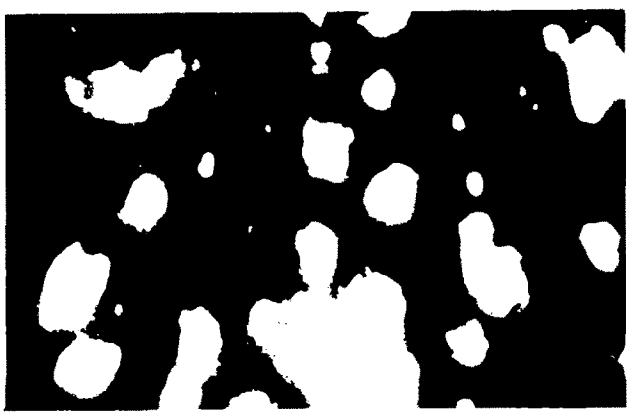


(a)

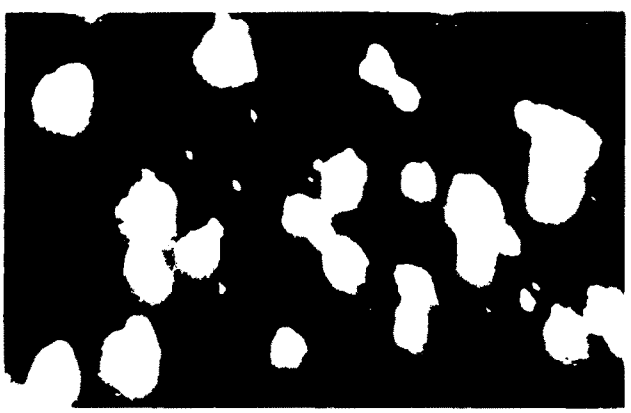


(b)

Fig. 6.3 Single hole breakdown patterns of (a) Pani-EB and (b) acid doped Pani films



(c)



(d)

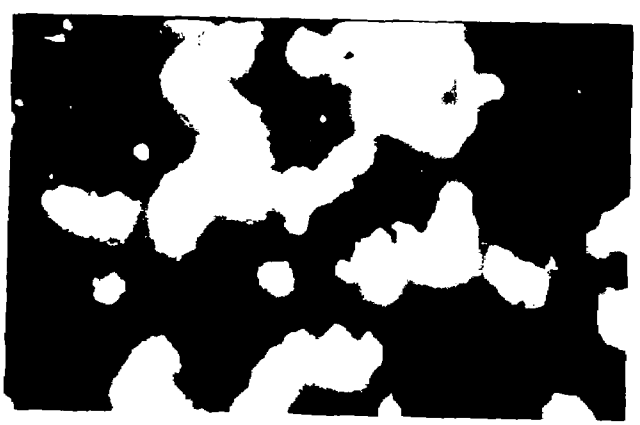
Fig. 6.3 Single hole breakdown patterns of (c) PPY and (d) PPY/Pani-EB blend films

doped Pani, PPY and PPY/Pani-EB films. The single hole breakdown originates from the cathode due to electronic impact ionization and terminates at the anode, due to successive avalanche in the same spot thereby increasing the local temperature. Due to the low thermal conductivity of the dielectric material, the dissipation of the thermal energy is low and hence there arises a rise of temperature that ultimately damages the dielectric. When the field is high at a flaw in the dielectric a large increase in current occurs. A relatively conducting channel appears then at the flaw through which the capacitor discharges, causing the observed rapid destruction in an explosive manner [31].

Figs.6.4 (a-d) show the propagating breakdown patterns for Pani-EB acid doped Pani, PPY and PPY/Pani-EB films. The propagating breakdown consists of consecutive repetitions of many single hole breakdowns. The mechanism for this propagation may be the following [32]. The breakdown hole periphery is very hot at the end of a single hole breakdown and the dielectric strength is therefore strongly reduced. When the series resistor is low and the source voltage is high, the capacitor recharges before the periphery cools down and a second breakdown occurs even before the capacitor is fully recharged. This chain continues and the breakdown propagates further.

Figs. 6.5 (a-d) show the complete breakdown patterns for pure Pani-EB and PPY films. Also it has been observed that the effect of breakdown is always greater at the edges inspite of the reinforcement of insulating layer.

(a)



(b)

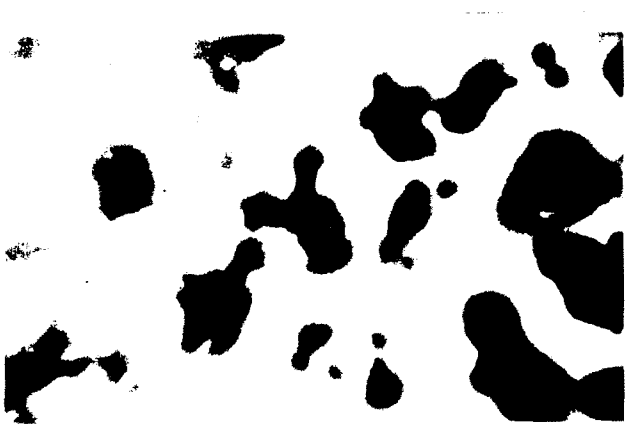
Fig. 6.4 Propagating breakdown patterns of (a) Pani-EB and (b) acid doped Pani films

(c)

(d)

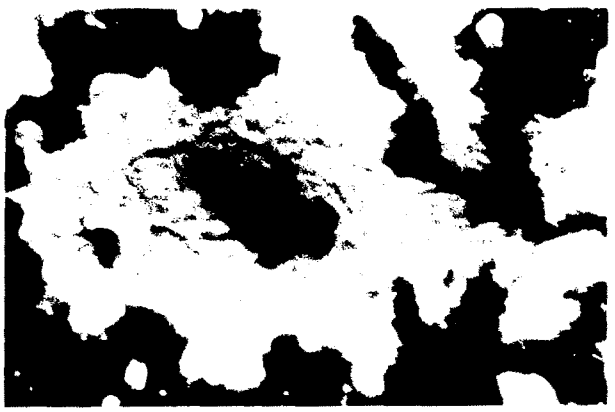
Fig. 6.4 Propagating breakdown patterns of (c) PPY and (d) PPY/Pani-EB blend films

(a)



(b)

Fig. 6.5 Complete breakdown patterns of (a) Pani-EB and (b) acid doped pani films



(c)

(d)

Fig. 6.5 Complete breakdown patterns of (c) PPY and (d) PPY/Pani-EB blend films

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