CHAPTER V

STUDY OF ELECTRICAL BREAKDOWN OF SEMI-CONDUCTING ORGANIC MATERIALS
3.1 Introduction

In the present technical age very large number of semiconducting organic materials e.g. Polystyrene, Polyvinyl chloride-acetate, Polyisobutylene etc. are usually being used in the form of thin sheets for insulation purposes. Interesting study about the electrical conduction under weak and high field had been made by a number of workers. Tanaka and Inuishi \(^1\)(1968) and Tanaka \(^2\)(1970) have studied the high field conduction of polythene and they have interpreted their results as being due to a combination of structural defects and space charge.

The dielectric breakdown of polymers has been reviewed by Whitehead \(^3\)(1951) and Mason \(^4\)(1959). Polythene which is composed of very long paraffin chain, has an electric electric strength similar to that of paraffin wax. Austen and Pelzer \(^5\), Oakes \(^6\) and Bird and Pelzer \(^7\) had obtained very similar field strength values for polythene, all of which lie in the range 6.5 - 7.3 \(\times 10^5\) V/cm.

For chlorinated polythene, Oakes found the highest values at low temperature, as in the case of amorphous materials. The highest electric strength was about \(11.5 \times 10^5\) V/cm. Similarly, Austen and Pelzer found that the low temperature
electric strength of amorphous polyvinyl chloride-acetate (vinylite) was also much greater than that of polythene, viz., $10^{-15} \times 10^6$ V/cm with a mean of about $12 \times 10^5$ V/cm.

For polystyrene which again is a hydrocarbon, the electric strength accordingly to Austen and Pelzer and also Oakes, is still of an order similar to polythene in the range $6-7.5 \times 10^6$ V/cm and there was no large increase in the low temperature range. Polystyrene was considered to be amorphous with respect to polythene (crystalline) in the low temperature region, while in the intermediate temperature region it behaves as crystalline with respect to polythene.

Breakdown strength as a function of temperature is of the same general form for all polymers. It is almost constant at low temperatures, falling off rapidly above some critical temperature. Recently the temperature dependence of breakdown strength for the usual type of recessed sample was measured by Lawson (1966). Bradwell, Cooper and Varlow (1971) investigated the high field conduction and breakdown of high purity polythene at 20°C.

The breakdown mechanism in a strongly divergent field may differ in details from that for an uniform field, but there is no reason for believing it to be fundamentally different.
Cooper and Grossart\textsuperscript{10} and Cooper and Wallace\textsuperscript{11} observed the channel direction about point electrodes impressed against the plates of potassium chloride and sodium chloride. The radius of the tip of the point was about 0.01 cm and the distance between the point and the opposing plane electrode was about 0.4 cm, so that an approximation to a spherically symmetrical field was obtained.

5.2 Experimental procedure and sample preparation

The experimental procedures and sample preparations have been described in Chapter II.

5.3 Details of measurements

\hspace{1cm} (A) Study under uniform field

(1) A comparison of electric breakdown strength of polystyrene and polyvinyl chloride-acetate with respect to polythene in the temperature range from 0\degree\textsuperscript{o} to 100\degree\textsuperscript{C} was made. Their breakdown strengths were determined in the above temperature range and breakdown strength Vs. temperature characteristics were plotted as shown in Fig. 5.1 and 5.2.

(2) The breakdown strength of polythene as a function of temperature with various admixtures of chlorine gas, was determined as shown in Fig. 5.3.
Study under non-uniform field i.e. divergent field

(1) Effect of temperature

In specimens with point-plane electrodes, breakdown is assumed to be initiated at the point electrode. When the effective stress at the point attains the fundamental electric strength of the specimen, breakdown occurs, hence corresponding effective field strength is known as average breakdown field strength which is much less than the fundamental electric strength (breakdown strength under uniform field).

The average breakdown strength of polythene was measured with point-plane electrodes in the temperature range 0°-100°C. The polarity effect was also investigated in the same range of temperature as shown in Fig. 5.4.

(2) Effect of thickness

The average electric strength of polythene is also measured with different gap separation of point-plane electrodes. Thus variation of thickness together with the polarity effect on the breakdown strength of polythene were measured at two temperatures : (a) 25°C and (b) 75°C as shown in Figs. 5.5 and 5.6 respectively.
Fig. 5.1 - The breakdown strength of polystyrene and polythene with temperature.
(3) Effect of radius of point electrode

Different rates of variation in the electric field across the gap can be obtained by varying the radius of the point electrode. The average electric breakdown strength of polythene between point-plane electrodes was measured with different electrode radius. The experiment was repeated at different temperatures and with polarity change of electrodes. The observations are shown in Figs. 5.7 and 5.8.

5.4 Results

(1) From Fig. 5.1 the following inferences can be drawn :-

(i) The temperature dependence of the breakdown strengths of polythene and polystyrene in the intermediate temperature range (0°C to 100°C) is found to vary in a similar manner as the breakdown strengths of silica glass and crystalline quartz measured by Von Hippel and Maurer 12 (1941).

(ii) The breakdown strength of polythene is constant upto 30°C temperature but it falls very steeply thereafter. For polystyrene the breakdown strength is constant over a very long range temperature (upto 75°C) and then falls sharply.
Fig. 5.2 – The breakdown strength of polyvinyl chloride acetate and polythene with temperature.
Fig. 5.3 - Effect of chlorination on electric strength of polythene.
Fig. 5.4 - The average electric strength of polythene between steel point-plane electrodes varies with temperature. (Radius of the point electrode is 25 μm.)
(iii) The characteristic curves intersect each other at 54°C temperature and thereafter the breakdown strength of polythene falls at a more rapid rate than for polystyrene.

(2) Similar results with polythene and polyvinyl chloride acetate are obtained as shown in Fig. 5.2.

(3) From Fig. 5.3 the following inferences can be drawn:

(i) In the intermediate temperature range, the chlorinated polythene has lower breakdown strength than that of pure polythene (after 20°C temperature).

(ii) The higher degree of chlorination further reduces the electric breakdown strength value in the above temperature range (after 20°C temperature).

It may be interesting to note that the above results can be compared with results already obtained in Chapter IV (page 30) for variation of the breakdown strength of NaCl as a function of temperature with various admixtures of AgCl after the critical temperature.

(4) Effect of temperature

From Fig. 5.4 the following inferences can be drawn:

(i) The effect of temperature on average electric strength
Fig. 5.5—The average electric strength of polythene between steel point plane electrodes varies with gap length separation at 25°C temperature.
Fig. 5.6 - The average electric strength of polythene between steel point plane electrodes varies with gap length separation at 75°C temperature.
Fig. 5.7 — The average electric strength of polythene between steel point plane electrodes varies with radius at 25°C temperature.
Fig. 5.8 - The average electric strength of polythene between steel point plane electrodes varies with radius at 75°C temperature.
is greater with a negative point than with a positive point, e.g., at room temperature the average electric strength for a given electrode configuration is nearly 25% greater with a negative than with a positive point.

(ii) The polarity effect decreases with rising temperature and it is negligible above 90°C.

(iii) In the intermediate temperature range the average breakdown strength of polythene decreases sharply with increasing temperature.

(5) Effect of thickness

From Figs. 5.5 and 5.6 the following inferences may be drawn:

The average breakdown strength of polythene decreases with increase of the thickness in a manner similar to that for thin film of alkali halides. It may also be further noted that —

(i) For thick samples the breakdown strength varies slowly as the thickness is increased.

(ii) For thin samples the variation is more rapid.

(6) Effect of radius of the point electrode

From Figs. 5.7 and 5.8 following results are obtained.

The average breakdown strength increases with increase of radius of the point electrode.
However,

(i) At room temperature, the variation is extremely slow for small radii of the electrodes, while the value increases very fast as one goes to higher values of electrode radii.

(ii) At higher temperature (75°C) the variation is extremely small for the entire range as shown in Fig. 5.6.

5.5 Discussion

The experimental values of breakdown strength of polythene, polystyrene and polyvinyl chloride acetate are similar to those obtained by Austen, Pelzer and Oakes within 10% variation (higher) at room temperature. The variation may be attributed to the short chain effect (vide supra, page 96) which becomes significant due to the possible formation of random oriented polycrystals in the liquid film samples, since electric strength depends mainly on the degree of crystallinity and the random orientation with respect to the breakdown field.

The present studies also show crystalline to amorphous behaviour amongst them. It follows from the work of Von Hippel and Maurer (1941) on quartz and silica that at low temperature
the amorphous form should have a higher electric strength than the crystalline form. The electric strength of quartz increases with the increase in temperature, while the value of electric breakdown strength for the silica falls with temperature. Similar observations for polythene, polystyrene and polyvinyl chloride acetate are reported in Figs. 5.1 and 5.2. The observations in Fig. 5.2 show that the liquid film of polyvinyl chloride acetate has a higher electric strength than the liquid film of polythene below 25°C. The latter maintains its electric strength upto 40°C beyond which the value falls rapidly, while the electric strength for polyvinyl chloride acetate falls continuously in this temperature range. This shows a good crystalline to amorphous behaviour between polythene and polyvinyl chloride acetate, the latter has a constitution similar to that of former except that some of hydrogen atoms are replaced by chlorine or acetyl group. It may be interesting to mention here the structural configuration of polythene and polyvinyl chloride acetate (as shown below):

\[
\begin{array}{ccccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{X} \\
\text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{X} \\
\text{H} & \text{X} & \text{H} & \text{X} & \text{H}
\end{array}
\]

General form of Hydrocarbon chains

\[X \text{ is H for polythene} \quad \text{X is Cl or } -\text{C-C} \quad \text{for } \text{CH}_3\]

The explanation is similar to the disorder or amorphous
form of the material as described in Chapter IV (page 81).

Frohlich has explained the gain and loss of energy of an
electron with the crystal lattice in terms of relaxation time
$\tau$ and electron energy $E$, as explained (vide infra). An
ordered oriented chain compound, e.g., paraffin has a structure
similar to that of a non-polar crystal. If the chain length
exceeds the mean free path, the end is a kind of defect and
decrease of chain length with increase of the electric field
strength by multiplication of defects. If the chain is very
short compared with the mean free path, the effective electron
mass would increase and as explained by Frohlich,\textsuperscript{13} the
breakdown strength would increase as the chains become shorter.

However, in case of very long chains, the effects of
the ends would not be great so that all such materials with a
similar chain and no dipolar groups should have a similar
electric strength. Polythene should therefore have an electric
strength similar to that of paraffins. The present observations
of polythene give a value of the order of $7 \times 10^6$ V/cm which is
similar to that for paraffins as reported in the literature.
Polyvinyl chloride acetate, however, gives higher values. This
is due to the dipolar radicals such as chlorine or acetate
group which provides an additional scattering agency similar
to defects in crystals as explained earlier (Page 85). The
structure of this material is amorphous as compared to polythene.

Similar observations are reported in Fig. 5.3 on
chlorinated polythene. The breakdown strength of polythene with different degrees of chlorination could also be explained on similar lines as explained above. Oakes found the highest values for chlorinated polythene at low temperature, as in the case of amorphous materials. Further he showed that the breakdown strength of polythene varies as a function of temperature with various admixtures of chlorine atoms. He also found that in low temperature region, the admixture of chlorine very greatly raises the breakdown strength, and at intermediate temperature, the effect is reversed after a cross-over. The present observations Fig. 5.3 are essentially similar to them. Higher degree of chlorination may make the material more amorphous thereby decreasing the electric strength more rapidly in the intermediate temperature range.

A very similar result had been obtained by Von Hippel and Maurer on solution of AgCl in NaCl. Keller had also obtained curves like those of Fig. 5.3 for NaCl in the above temperature range.

This may be due to the successive replacement of some of the Na atoms by Ag. Thus qualitative confirmation of crystalline and amorphous behaviour with admixture of foreign ions has been found both in a simple polar polycrystal and long chain polymer.
Effect of temperature

Fig. 5.4 shows that the average electric strength of polythene between point and plane electrodes varies with temperature in a manner similar to the fundamental electric strength.

As a criterion for breakdown in crystals Von Hippel suggested that free electrons must gain more energy from the applied than they lose in collision with the lattice. This theory modified and extended to amorphous materials by Frohlich, predicts that :-

(i) at low temperatures very high stress is necessary to cause breakdown because there are few free electrons available to initiate avalanche (Ref. Page 75). The presence of dipoles or defects in lattice, which decrease the mean free path of the electrons would further increase the stress required.

(ii) Above a critical temperature, the electric strength would decrease with rising temperature. This is because the number of electrons, both in the conduction band and trapped in imperfection levels, increase with rising temperature (as described in Chapter IV, page 85). A lower stress is then required to initiate breakdown.
Fig. 5.1 to 5.4 indicate a similarity in the behaviour, showing a fall in the breakdown strength above the critical temperature.

In case of non-uniform field, higher stress is required for breakdown when the point is made negative than when it is positive Fig. 5.4. The difference is ascribed to the decrease in stress around the point, due to field emission of electrons which form a space charge extension of the point. Although space charge will also form around a positive point, it is likely to be limited by smaller number of free electrons moving towards the point, so that the reduction in stress near it will be smaller than that for the negative point. With the rise in temperature, the negative-carrier (electron) mobility continuously exceeds that of the corresponding positive carriers. This results in minimising the difference in the average electric breakdown strength as compared to that at room temperature. The present observations are in accordance with this.

**Effect of thickness**

The breakdown strength varies as $d^{-1/2}$ where $d$ is dielectric thickness in accordance with Eqn. (1.35). This behaviour is in agreement with the theory of Forlani and
Minnaja, taking into account of the avalanche multiplication.

Figs. 5.5 and 5.6 show that the electric strength of polythene increases with decrease of thickness much more sharply than that required by Frohlich's theory.

Effect of radius of point electrode

Fig. 5.7 shows that variation of average electric strength with the radius of the point electrode. It is well known that sharper the point electrode, stronger is the divergent field. The theory of intrinsic breakdown predicts an increase in conductivity with field strength. The conductivity of polythene in the highly stress region near the point is greater than in the bulk of the material so that the effective stress near the point is reduced. Mason (1959) gave an empirical equation which relates the maximum breakdown strength $F_m$ and average breakdown strength $F_{av}$ thus,

$$F_{max} = \frac{2 F_{av} d}{r \log (1 + \frac{4d}{r})}$$

However, from above equation the greatest reduction in average breakdown strength is to be expected when $\frac{r}{d}$ is small. For a given value of $d$, the ratio $\frac{F_{max}}{F_{av}}$ is expected to be much
larger for smaller points than for larger points, as is found experimentally; Figs. 5.7. Fig. 5.8 gives the lower values of average field strength in comparison with Fig. 5.7. This may be interpreted as due to thermal breakdown under the present circumstances. Thin films of polythene set up in such a way as to have poor heat-dissipation properties may be expected to breakdown thermally at the given intermediate temperature (75°C).
REFERENCES


5 Austen and Pelzer. (1946), Dielectric breakdown of solid insulation, Prog. Dielect. 93, part 1, 525.


