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THE INFLUENCE OF TITANIUM DIOXIDE ADDITIVE ON THE SHORT-TERM D.C. BREAKDOWN STRENGTH OF POLYETHYLENE

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Abstract.

The effect of the addition of 1% by weight of titanium dioxide fine particles to low density polyethylene (LDPE) on the short-term d.c. breakdown strength of the LDPE was investigated using direct and reverse polarity voltages. The samples used, were cylinders of both plain and doped materials, with hemispherically tipped cylindrical electrodes completely embedded in the material, with a minimum gap length between the electrodes tips of 0.25 mm. All tests were conducted at room temperature.

Results indicate that although the addition of TiO₂ has reduced the d.c. breakdown strength of the doped material if compared to the plain material, yet it has significantly improved its d.c. reverse polarity characteristics. The doped material seems to be insensitive to the d.c. polarity reversals. The observed beneficial effect of the addition of TiO₂ on the d.c. reverse polarity characteristics is attributed to the role of this additive in modifying the trapping levels in the polymer, and the consequent change in the space charge pattern in the doped material.

Introduction.

Despite the unique advantages of using polymeric insulation for high voltage d.c. cables, such cables do pose some problems to cable designers. D.C. breakdown tests on experimental polyethylene (PE) and crosslinked polyethylene (XLPE) cables have shown that the d.c. breakdown strength with polarity reversal is significantly less than the d.c. breakdown strength without polarity reversal. The reduction in the breakdown strength with polarity reversals was attributed to the formation of space charges in the polymer [1,2].

Several methods, including the use of additives, have been suggested to suppress the space charge effects in polymers. [3,4]. None of these methods, however, has been reported to give a conclusive solution to the problem.

Earlier space charge observations by Khalil et.al. [5] have indicated that the addition of fine particles of titanium dioxide (TiO₂) to LDPE has a significant effect on the space charge distribution in the doped material compared to the plain material.

In the present work, the effect of adding 1 wt% of TiO₂ fine particles to LDPE on the d.c. breakdown strength of LDPE is investigated under both direct and reverse polarity conditions.

Experimental Details.

For these measurements, special cylindrical test samples were used as shown in Fig. 1. Two hemispherically tipped stainless steel electrodes were embedded in the investigated material by moulding. The special mould design allowed the adjustment of the gap between the tips of the electrodes. Since the main aim of these measurements was to determine the electric breakdown of the investigated material, special efforts were made to exclude the effects of the different factors on the accuracy of the results such as the edge effects, purity and cleanliness of the material and electrodes. 64 samples were used in this investigation: 34 samples of plain LDPE and 30 samples of 1 wt% TiO₂ doped LDPE. The LDPE was of AT0 Chemie, France, 1002 CJV of density of 0.925 g/cm³. The doped material of LDPE + TiO₂ was prepared by the Technological Institute in Denmark. The samples of each material were divided into two groups, the mean value of the gap length in all the groups was 0.25 mm with a standard deviation of 0.03 mm.

Fig. 1. Configuration of breakdown test sample.
Breakdown tests were performed using two different voltage applications. The first was stepwise increasing the voltage. In this case the voltage was raised in steps, each 30 kV, and the sample was left for 10 minutes on that level before the voltage was raised again to the next step until breakdown. The second method of voltage application was stepwise increasing with polarity reversal. In this case the polarity was reversed each time before the voltage was raised to the next level. Polarity reversal was achieved by the mechanical reversal of the position of the sample with respect to the d.c. supply terminals in the oil basin. All breakdown tests were performed at room temperature.

**Results and Discussion**

Table 1 shows the effect of doping the LDPE with 1 wt% TiO₂ on the d.c. breakdown characteristics of the doped material in comparison with the corresponding characteristics of plain LDPE.

**Table 1**

Effect of doping LDPE with 1 wt% of TiO₂ on the d.c. breakdown strength of the doped material.

<table>
<thead>
<tr>
<th>Method of voltage Application</th>
<th>Breakdown Strength MV cm⁻¹ (mean value)</th>
<th>Effect of polarity reversal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Direct polarity</td>
<td>Reverse polarity</td>
</tr>
<tr>
<td>Plain LDPE</td>
<td>7.1 (0.6)*</td>
<td>6.4 (0.9)*</td>
</tr>
<tr>
<td>TiO₂ doped LDPE</td>
<td>6.5 (0.5)*</td>
<td>6.3 (0.7)*</td>
</tr>
<tr>
<td>Effect of doping with TiO₂</td>
<td>0.91</td>
<td>0.98</td>
</tr>
</tbody>
</table>

$* $ standard deviation values.

Effect of doping with 1 wt% TiO₂ on the d.c. breakdown strength of LDPE.

This effect is expressed as the ratio:

\[
\frac{E_{BD}}{E_{BP}}
\]

As shown from table 1, this ratio is equal to 0.91, and 0.98 at direct and reverse polarity conditions respectively.

Statistical analysis using the t-distribution tests [6], has shown that the reduction in the breakdown strength due to the addition of TiO₂, is statistically significant at 95% level of significance, in case of direct polarity. In case of reverse polarity the reduction was found insignificant on the same level.
Effect of doping with 1 wt% TiO$_2$ on the reverse polarity breakdown strength.

The effect of polarity reversal on the d.c. breakdown strength can be evaluated by the ratio:

\[
\frac{\text{Breakdown strength with reverse polarity}}{\text{Breakdown strength with direct polarity}} = \frac{E_{\text{BRP}}}{E_{\text{BDP}}}
\]

From Table 1, it is evident that this ratio is increased from 0.90 in case of plain LDPE to 0.97 in case of LDPE + TiO$_2$. Moreover, statistical analysis of the breakdown data shows that in the doped material, the difference between the breakdown values with direct polarity and reverse polarity is statistically insignificant at 95% level of significance while the corresponding difference in plain LDPE is significant at the same level.

Thus it seems that the addition of TiO$_2$ has markedly improved the d.c. reverse polarity breakdown strength of the doped material.

The reduction in the d.c. breakdown strength upon polarity reversal in LDPE and XLPE is usually attributed to space charge accumulation in the polymer [1,2].

In PE, the space charge distribution is generally of homocharge type, negative at the cathode and positive at the anode [1,7,8].

With homocharge distribution the field near the electrodes is relieved and subsequent charge carrier injection is suppressed.

The d.c. breakdown strength in this case is increased. If the polarity of the voltage is reversed, the space charge is frozen in, the field will be enhanced at both electrodes and the material will breakdown at a lower voltage. The present results for plain LDPE seem to coincide with this picture.

With TiO$_2$ as an additive, the breakdown strength is generally reduced. It is interesting to notice that such a reduction in the breakdown strength is dependent on the method of voltage application. With direct polarity the reduction is about 9% and is considered significant while with reverse polarity, the reduction is only by 2% and is insignificant.

TiO$_2$ is considered to be an n-type excess metal semiconductor with Ti ions and electrons occupying interstitial positions [9]. The addition of TiO$_2$ may result in modifying the trapping levels in the polymer [10,11], and consequently modifying the space charge distribution in the doped material. Space charge formation in polymers is known to be closely related to the nature of traps [12,13]. Earlier observations of space charge, using the field probe technique have shown that the addition of TiO$_2$ to LDPE has resulted in the complete change of the pattern of space charge distribution from a balanced homocharge distribution in the plain material to a negative charge dominated distribution in the doped material [5].

The departure of the space charge distribution from a homocharge type in the plain material, due to the addition of TiO$_2$, may result in the reduction of the d.c. breakdown strength of the doped material, due to the field enhancement at one of the electrodes. With reverse polarity, the space charge will still be frozen in, while the electrodes will interchange their roles, and the field enhancement will be on the other electrode giving the same breakdown probability. This picture is in agreement with the present breakdown results in the TiO$_2$ doped LDPE.

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