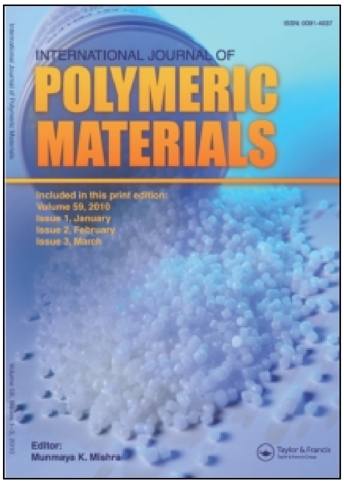

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# On the Effects of $TiO_2$ Additive on D.C. Conductivity and Morphology of Polyethylene

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# On the Effects of $TiO_2$ Additive on D.C. Conductivity and Morphology of Polyethylene

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The effects of doping low density polyethylene (LDPE) with fine particles of $TiO_2$ as an inorganic additive on the d.c. conductivity and morphology of LDPE were investigated using two temperature profiles: the first at constant temperature of 40°C and the second under thermal cycling between 40°C and 80°C in the presence of an electric field. Results indicate that the incorporation of $TiO_2$ in the polymer has increased the charge carrier mobility and the d.c. conductivity of the doped LDPE. Morphological investigations using scanning electron microscopy (SEM) of $CCl_4$ vapour etched surfaces of the undoped and doped materials show that the addition of the inorganic additive to LDPE has considerably changed the morphology of the polymer. It is also shown that the morphology of the doped LDPE has undergone considerable structural changes after thermal cycling in the presence of the d.c. electric field during d.c. conductivity measurements. The role of the additive in increasing the d.c. conductivity and changing the morphology of LDPE is discussed. An attempt is made to correlate between the recorded increase in the d.c. conductivity and the observed morphological changes in the investigated material.

*Keywords:* Electrical conductivity; d.c. conductivity; polyethylene; additives; morphology; $TiO_2$

## INTRODUCTION

The use of additives to materials like polyethylene (PE) has been one of the techniques to modify and/or improve the characteristics of this polymer for certain applications. In polymeric insulated cables, additives have been used to improve the resistance of the polymer to partial discharges, formation of water trees and manufacture of emission shields [1,2]. Additives have also been used to suppress the build-up of space charges in polymeric materials used for developing high voltage d.c. cables. The use of titanium dioxide additive to LDPE was found to have beneficial effects on space charge accumulation as well as on d.c. breakdown strength of LDPE [3–5]. Another use of additives to polymers is to provide an insight into the nature and origin of charge carriers and charge transport mechanisms [6]. It has been shown that doping PE with halogens has significant effects on charge carrier mobilities, breakdown strength as well as space charge formation of the doped polymer [4,7]. The use of additives to polymers requires careful investigation of the effects of these additives on the host polymer characteristics in order to determine not only the beneficial effects of the additive on the composite polymer characteristics but also the possible negative effects of these additives in impairing the original characteristics of the undoped polymer. Additives to polymers are expected to influence, amongst other factors, the d.c. conductivity of the host polymer as well as its structure. The electrical conductivity in polymers has been addressed by several authors [8–18]. Few of those authors have investigated the relationship between the electrical conductivity of polymers and polymer structure and morphology [12–15]. Little attention has been given to study the effects of additives on either the d.c. conductivity or morphology of the doped material [16–18]. The objectives of the present investigation are: first, to determine the effects of titanium dioxide additive and thermal cycling on both the d.c. conductivity and the morphology of LDPE, second, to shed more light on the correlation between changes in polymer morphology and its d.c. conductivity.

## EXPERIMENTAL

Two types of materials were used in the present investigation: undoped LDPE and 1 wt% $TiO_2$ doped LDPE. Test samples were square plaques (190 × 190 × 2 mm) of LDPE (density 925 kg/m$^3$, melt index 0.25 gm/10 min) made by pressing from pellets. Mixing of the additive was accomplished by means of a double extruder prior to pressing. Conductivity samples were discs of 175 mm diameter cut from those plaques and provided with vacuum evaporated gold electrodes and guard rings.

In order to screen the samples and guarantee reproducibility of the results test samples were thermally and electrically conditioned before d.c. conductivity measurements were started. First, test samples were subjected to vacuum ($10^{-2}$ torr) for 24 hours after which they were mounted in a test cell and immersed in silicone oil, where they were electrically conditioned by subjecting them to 60 kV d.c. 24 hours at 40°C followed by another 24 hours with the electrodes shorted.

D.C. conductivity for undoped LDPE was investigated using constant temperature of 40°C for 4 days.

The effect of the additive on the d.c. conductivity was investigated using two different temperature profiles: (i) constant temperature equal 40°C for 4 days, (ii) thermal cycling between 80°C and 40°C for 10 days. During both periods a voltage of 50 kV d.c. was applied across the electrodes while the current flowing through the sample was monitored.

In order to determine the dependence of the current density $J$ on inverse of temperature $1/T$ ($J$ *versus* $1/T$) at constant electric field for both undoped and doped LDPE another temperature profile was used. In this case the voltage across the sample was kept at 50 kV. The current was measured and recorded at different temperature levels 80°C, 70°C, 65°C, 60°C, 55°C, 50°C and 40°C starting at 80°C. Each temperature level was left for 24 hours after which it was reduced to the next temperature level until it reached 40°C where the temperature was left for 48 hours after which the temperature profile was reversed in a similar manner but in an ascending order until temperature was reached 80°C. The average currents during the ascending and descending parts of the profile at temperature levels of 80°C, 70°C, 60°C and 50°C were used determine the dependence of ($J$ *versus* $1/T$).

The system used for d.c. conductivity measurements is described elsewhere [19, 20].

Structural and morphological investigations were conducted by SEM of etched surfaces using $CCl_4$ vapour. Three groups of samples were used for these investigations. The first two groups were cut from the corners of the undoped and doped samples prior to being subjected to any thermal or electrical conditioning or conductivity measurements. The third group was cut from the doped sample after conditioning and d.c. conductivity measurements with thermal cycling. For SEM investigations two samples were used from each group: one sample having the size of 10 × 10 mm and another having the size 10 × 5 mm. The samples were embedded in a cold mounting resin and wet ground using standard metallurgical technique and then polished. Etching was effected using $CCl_4$ vapour to reflux on the surface of the sample for a short period (30–90 seconds) to avoid swelling of the sample. Repercipitation of the solvated resin on the sample polished surface was avoided by keeping the surface vertical in the vapour. The etched samples were then dried under vacuum for 24 hours and coated by 50 μm platinum layer. SEM was carried out using a JEOL-JSM-03 instrument.

## RESULTS AND DISCUSSION

Figure 1a shows the current–time dependence for undoped LDPE during the first run of conductivity measurements at constant temperature of 40°C. From this figure it can be seen that the current passes through a well defined peak value of 2.5 nA after about 8000 s and then rapidly decays towards a quasi-steady state value of about 0.2 nA. Figure 1b shows the current time dependence for doped LDPE during the first run of conductivity measurements at constant temperature of 40°C. In this case the current passes through a less defined peak value of about 3.8 nA after a time period of about 2500 s after which it decays slowly to a value of about 2 nA after 4 days. The observed current maxima show similarities with the current transients in solid dielectrics previously observed by different authors [11, 21–24]. A rough estimate of the charge carrier mobility "$\mu_{\mathrm{eff}}$" can be obtained from the time of the current maximum $t_m$ using the equation:

$$\mu_{\mathrm{eff}} = 0.786\, a^2/Vt_m \quad \mathrm{cm^2V^{-1}s^{-1}}$$

where $V$ = the applied voltage, $a$ = sample thickness in cm and $t_m$ = the time of the current maximum [21, 22]. This formula was used to calculate the effective mobility of charge carriers in both the doped and undoped materials as shown in Table I.

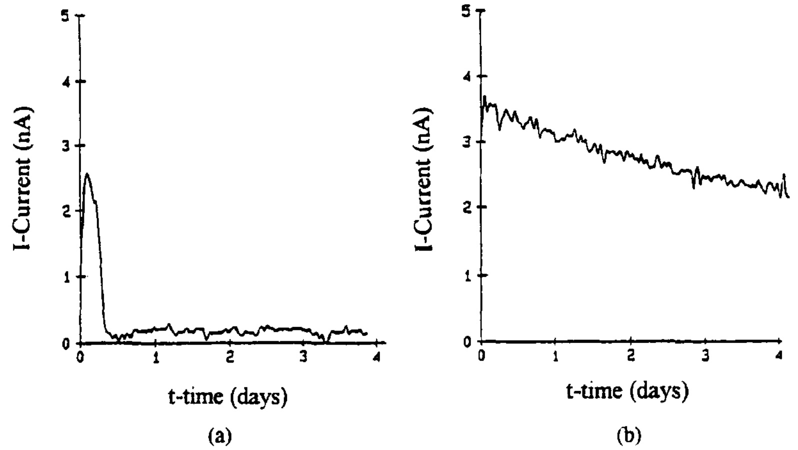


FIGURE 1 The current–time dependence during the first run of conductivity measurements at constant temperature of 40°C: (a) undoped LDPE, (b) 1 wt% TiO$_2$ doped LDPE.

TABLE I Effect of TiO$_2$ on effective mobility of charge carriers in LDPE using d.c. transients theory

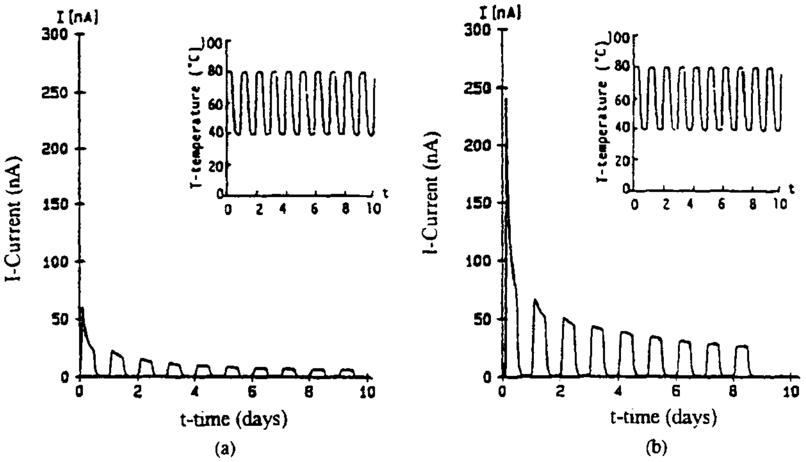
| *Material* | $\mu_{eff}$ $(cm^2 V^{-1} s^{-1})$ |
|---|---|
| Undoped LDPE | $7 \times 10^{-11}$ |
| TiO$_2$ doped LDPE | $22.4 \times 10^{-11}$ |

From Table I it is evident that the addition of 1 wt% TiO$_2$ to LDPE has increased the effective mobility of the charge carriers in the doped material by a factor of about 3 compared to the undoped material. A comparison between the value of the effective charge carrier mobility in LDPE calculated from the present work and corresponding values determined by different authors using different techniques is made as shown in Table II. It is evident from Table II that the effective charge carrier mobility in LDPE calculated from the present work compares reasonably with the values previously reported by other authors [22–24].

Figures 2a and 2b depict the current–time dependencies during thermal cycling between 40°C and 80°C for undoped LDPE and 1 wt% TiO$_2$ respectively. The thermal cycling profiles are shown in the inserts. For the undoped LDPE the current reaches to a maximum value of 64 nA during the first period of thermal cycling and then

TABLE II Comparison between the present value of effective charge carrier mobility in LDPE and corresponding values previously determined by different authors

| *Reference* | *Technique and materials used* | *Charge carrier mobility* ($cm^2 V^{-1} s^{-1}$) |
|---|---|---|
| Present Work | D.C. Transients, LDPE | $7 \times 10^{-11}$ ($T = 40°C$) |
| Fischer and Rohl [22] | D.C. Transients in oxidized LDPE | $7 \times 10^{-11}$–$2 \times 10^{-11}$ ($T = 71°C$) |
| Ieda *et al.* [23] | D.C. Transients in plain LDPE, oxidized LDPE and HDPE | $10^{-11} - 10^{-8}$ ($T = 40°C - 80°C$) |
| H. St. Onge [24] | D.C. Transients in graphite loaded LDPE | $10^{-11} - 10^{-9}$ ($T = 60°C) - 120°C$) |
| Davies [25] | Surface charge decay | $10^{-10} - 10^{-8}$ ($T = 70°C$) |
| Tanaka and Calderwood [26] | Photo-current investigation | $10^{-4}$ ($T = 20°C$) |



(a)

(b)

FIGURE 2 Current–time dependencies during thermal cycling between 40°C and 80°C: (a) undoped LDPE (b) 1 wt% $TiO_2$ doped LDPE.

decays to a quasi-steady state value of about 6 nA after about 5 days of the cycling period. For the 1 wt% $TiO_2$ doped LDPE the maximum current level reached is 240 nA and the quasi-steady value is 20 nA which is reached after about 7 days. Thus, under transient conditions the achieved maximum current in the doped material is about 3.75 the corresponding value in the undoped material while at steady state conditions this factor is 3.3. The volume conductivity for each material can be calculated using the formula:

$$\sigma_v = ai/AV \quad (\mathrm{S\,m^{-1}})$$

where $A$ is the crossectional area of the electrodes, $V$ the applied voltage, $a$ is the sample thickness and $i$ is the achieved quasi-steady state current.

The values of the volume conductivity in each case are shown in Table III. From Table III it is evident that the addition of 1 wt% $TiO_2$ to LDPE has increased its volume conductivity by a factor of about 3.

In Figure 3 a comparison is given between the log current density *versus* $1/T$ dependencies for undoped and 1 wt% $TiO_2$ doped LDPE at a constant electric field of 27.7 kV/mm. For the undoped LDPE the dependence of the log current density $J$ *versus* $1/T$ obeys an Arrhenius law. In this case the conductivity of LDPE is thermally activated with an energy of about 0.76 ev. This value compares well with some other previously reported values [27, 28]. In Table IV the various activation energies of LDPE reported by other authors are compared with the value determined in the present work.

According to Figure 3, the log current density *versus* $1/T$ (Log $J$ *versus* $1/T$) dependence for 1 wt% $TiO_2$ doped LDPE does not obey the Arrhenius equation. In this case the (Log $J$ *versus* $1/T$) dependence changes the slope at about 63°C and it is not possible to obtain a single activation energy from these plots. These results are in general agreement with the previously reported results of other authors [18]. Similar changes of the (Log $J$ *versus* $1/T$) dependence were observed before for Teflon (FEP) and polyethylene terephthalate (PET) during investigating the conductivity using corona electrodes. The authors of that work have shown that for PET, the temperature at which the (Log $J$ *versus* $1/T$) dependence changes the slope coincides with the glass transition temperature of PET. The change of the slope was attributed to the ionic conduction which was shown before to play an important

TABLE III Effect of doping LDPE with 1wt% $TiO_2$ on the volume conductivity of the doped material

| *Materials* | *Conductivity* ($S\ m^{-1}$) |
|---|---|
| Undoped LDPE | $0.5 \times 10^{-16}$ |
| 1 wt% $TiO_2$ doped LDPE | $1.6 \times 10^{-16}$ |

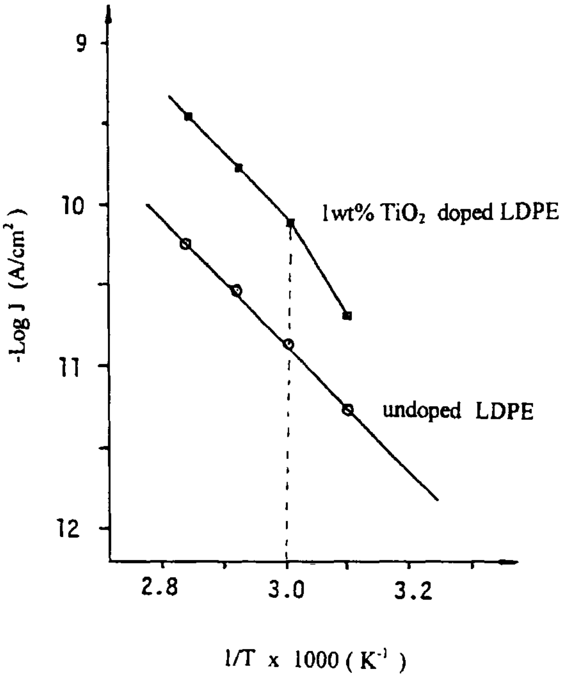


FIGURE 3 Log current density *versus* $1/T$ for undoped and 1 wt% $TiO_2$ doped LDPE at a constant electric field.

TABLE IV Comparison between the present value of the activation energy in LDPE and corresponding values determined by different authors

| *Reference* | *Activation energy (ev)* | *Remarks* |
|---|---|---|
| Present work | 0.76 | Electric field ~ $2.8 \times 10^5\ V\,cm^{-1}$ |
| P. Rohl [27] | 1.00 | Electric field $(0.75 - 3.7) \times 10^5\ V\,cm^{-1}$ |
| Pellissou [28] | 0.58 – 0.95 | Electric field > $2 \times 10^5\ V\,cm^{-1}$ |

role in that temperature range. However, no explanation has been given for the observed change of the slope of the (Log $J$ *versus* $1/T$) dependence for FEP [29].

Figure 4a shows SEM micrographs for undoped LDPE prior to conditioning and d.c. conductivity measurements. The micrographs reveal spherulitic structures as well as lamellae accomodated within the spherulites typical for LDPE.

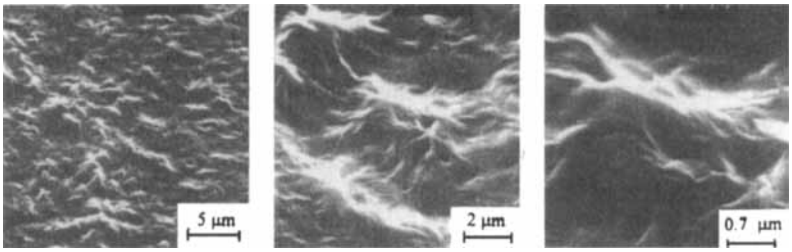


FIGURE 4a SEM micrographs for undoped LDPE prior to conditioning and d.c. conductivity measurements.

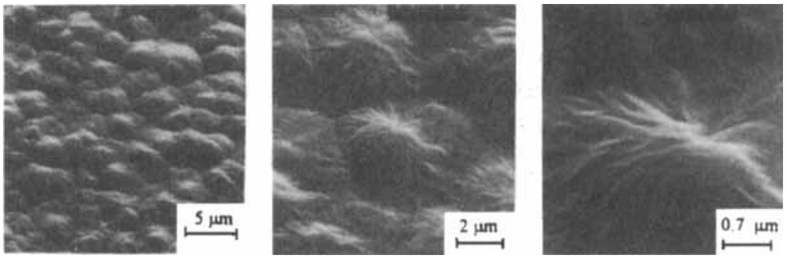


FIGURE 4b SEM micrographs for the 1 wt% $TiO_2$ doped LDPE prior to conditioning and d.c. conductivity measurements.

Figure 4b shows SEM micrographs for the 1 wt% $TiO_2$ doped LDPE prior to conditioning and d.c. conductivity measurements. In this case, the structure of the doped material exhibits a pronounced spherulitic structure with highly ordered lamellar structure within the spherulitic entities. It appears that the incorporation of the additive particles into the polymer has caused pronounced changes in the spherulite size, order and structure. The spherulites appear to be more homogeneous in size and shape between each other. Moreover, they exhibit well formed, larger size and higher degree of order compared to those of the undoped LDPE. The reason for this higher ordering in the spherulitic structure of the doped LDPE compared to the undoped LDPE can be attributed to the effects of the incorporation of the $TiO_2$ particles on the spherulite nucleation in the doped material. In most crystalline polymers, nucleation is heterogeneous in origin: the formation of primary nuclei is dominated by the presence of foreign matter (accidental presence or intentional incorporation) [30, 31].

Figure 4c shows SEM micrographs for the doped LDPE after being subjected to conditioning and d.c. conductivity measurements with thermal cycling. It is evident that the material structure has undergone considerable changes. The well formed spherulites previously observed in the sample, before being subjected to conditioning and thermal cycling under electrical stress, appear to be transformed into a structure of fibrillar appearance as a result of the combined thermal and electrical conditioning it was subjected to. The dependence of the structure of LDPE on heat treatment and combined thermal and electrical variations has been reported before by few authors [16, 32].

Although the knowledge of the electrical conduction process in polymers is still incomplete, the results of many workers suggest that in pure polyolefins the conduction is electronic in nature, the charge carriers are mainly electrons injected from the electrodes and the charge carrier transport mechanism is bulk-limited of hopping type. The hopping and trapping sites can be of various types depending on polymer structure and content of chemical heterogeneities. $C = C$ double bonds, $C = O$ and terminal vinyl groups have been postulated as hopping centers and/or trapping sites in such polymer [8–11]. The results of the present work are in general agreement with the above picture. The current–time characteristics in both the undoped and doped materials at constant temperature and under thermal cycling conditions show a pronounced peak (in case of the undoped LDPE) and a less pronounced peak (in case of the doped LDPE). This behaviour can be explained as follows: when the voltage is applied, charge carriers are injected at the electrodes (mainly electrons at the

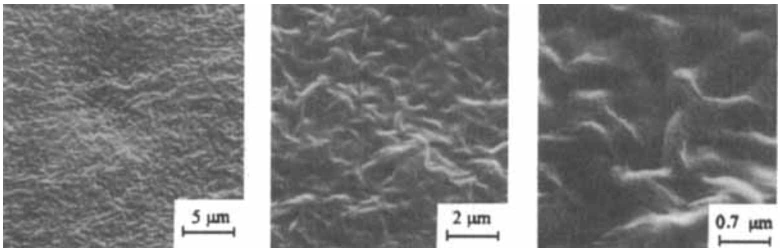


FIGURE 4c SEM micrographs for the doped LDPE after being subjected to conditioning and conductivity measurements.

cathode) and the current reaches its maximum value while the traps are rapidly filled forming a space charge which influences the field distribution at the electrodes and determines the magnitude of the flowing current. The phenomenon of current maxima in d.c. transients in some polymers including PE is explained by the build-up of space charge in the polymer [11, 21, 22]. The formation of space charge in PE under d.c. conditions is not inconsistent with the characteristics of such material. The build-up of space charge in undoped and doped LDPE under similar d.c. conditions has been reported by a number of authors using different techniques for direct observations of space charge [33–35].

The present results show that the incorporation of $TiO_2$ into LDPE produced a composite system which exhibited higher charge carrier mobility, higher electrical conductivity and a different morphology compared to the undoped material. A possible explanation for the role of $TiO_2$ can be as follows: $TiO_2$ is considered as *n*-type excess $Ti^{++++}$ ions and electrons occupying interstitial positions [36]. The introduction of $TiO_2$ may give rise to donor levels which will act as reducing agent to annihilate some of the defect sites thus reducing trapping and yielding the observed higher conduction current. Luminiscence studies have shown that metallic impurities such as titanium can modify the trapping effect by combining with the defect states and annihilating the trap center [37]. Moreover, $TiO_2$ was shown to have a significant effect on charge trapping and conductivity properties of linear LDPE [38]. Evidence from space charge measurements in undoped and $TiO_2$ doped LDPE indicate that the addition of $TiO_2$ to LDPE has resulted in reducing the magnitude of the accumulated space charge in the material and changed its distribution pattern if compared with the corresponding magnitude and distribution pattern for undoped LDPE [3]. The reduction of space charge in the doped material is expected to lead to higher conduction current as shown by the present results.

The hopping and trapping sites in materials like PE are usually assumed to be distributed in the amorphous regions between spherulites and specifically on the spherulite boundaries. The presence of spherulites influences the d.c. conductivity in a complicated manner. This is due to the fact that not only the size of the elements of morphological structure but also their degree of perfection contribute to the creation or annihilation of trapping sites of different energy levels. In the present work it is shown that the incorporation of $TiO_2$ particles in the polymer has influenced the morphology of the doped material by increasing the spherulite size and improving the morphological order. With the larger size of spherulites and much ordered structure the trapping sites are expected to be reduced giving rise to the observed increase of conductivity.

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