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ON THE EFFECT OF THE STRUCTURAL PROPERTIES OF POLYETHYLENE ON THE D.C. CONDUCTIVITY IN THE TEMPERATURE RANGE FROM 40°C TO 80°C.

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ABSTRACT

Measurements of the flowing current under the effect of d.c. fields were conducted using relatively thick samples (1.8 mm), of three different materials: plain low density polyethylene (LDPE), crosslinked polyethylene (XLPE) and 1wt% titanium dioxide (TiO₂) doped LDPE. The measurements were performed over a range of temperature from 40°C to 80°C and electric fields as high as 3 x 10⁵ V/cm. Results indicate that the observed d.c. conductive characteristics are different for the three materials. Those differences are attributed to the difference of the chemical and morphological structure of the used materials. Scanning electron micrographs seem to support this assumption.

INTRODUCTION

It has been long realized that the d.c. conductivity of polymers depends, amongst other factors, on the chemical composition as well as the physical structure of these materials [1]. However, few investigations have been dedicated to correlate between the morphological structure of the polymers and their electrical properties. [2, 3]. Principal among the reasons of such state of affairs may be the involved difficulties in using the structure characterization techniques to observe representative microstructures with the electron microscope.

In the present paper, an attempt is made to establish connection between the d.c. conductivity measurements for 3 different materials and the morphological structure of these materials. An etching technique is combined with SEM to reveal the microstructure of the used materials.
EXPERIMENTAL DETAILS

i) D.C. conductivity measurements.

The samples used for these measurements were discs of 175 mm diameter and 1.8 mm thick. They were cut from rectangular plates prepared by pressing from pellets. Details of these measurements are described elsewhere [4, 5].

ii) Scanning electronmicroscopy (SEM).

Samples for SEM investigations were prepared by cutting small pieces from the corners of the same plates from which the conductivity samples were cut. Those samples were not subjected to any thermal or electrical conditioning. The samples were polished and smoothed using standard metallurgical equipment. After polishing, etching was achieved by allowing carbon tetrachloride vapour to reflux on the surface for 30 to 90 seconds. The samples were then prepared for SEM by coating it by a layer of platinum of 50 Å thickness. Scanning electron microscopy was carried out using a JEOL JSM-O3 instrument. This technique has been described in more details by other authors [5].

RESULTS AND DISCUSSION

i) The current-time dependencies

Fig. 1 shows the current-time dependencies for: (a) LDPE, (b) XLPE and (c) 1wt% TiO₂ doped LDPE respectively. The patterns of the current variations are in qualitative similarity in the 3 materials. In each case the current exhibits a pronounced peak after the voltage application followed by a current decay in each cycle. By repetition of the cycles the magnitudes of the currents decrease, reaching almost steady state values, after several days. The doped material exhibits the maximum value of the currents while XLPE exhibits the minimum.

ii) The steady state currents against the inverse temperature.

Fig. 2 shows the Arrhenius plots of the steady state currents against the inverse of temperature in the 3 investigated materials. The plots for LDPE and XLPE are reasonably linear indicating a single activation energy of 0.76 e.v. and 0.95 e.v. respectively. As for LDPE + 1wt% TiO₂, the plots are not linear indicating that it is not possible to obtain a single activation energy from those plots. This is consistent with earlier findings by Damon et.al. [7]. It might be suggested that, in the case of the doped material, two activation energies can be obtained for two different temperature ranges. Further work will be continued to elucidate the behaviour of the TiO₂ doped material.
Fig. 1. The current-time dependencies for:
(a) plain LDPE, (b) XLPE, (c) LDPE + 1wt% TiO$_2$
Fig. 2. Arrhenius plots of steady state current against 1/T.

Fig. 3. Etched surfaces of
(a) plain LDPE
(b) XLPE
(c) LDPE + 1wt% TiO₂
(X 1500)
iii) Scanning electron micrographs.

Fig 3 shows the etched surfaces of the 3 investigated materials (before being subjected to any thermal or electrical conditioning). In fig. 3a, (plain LDPE), the morphology is that of typical spherulites, while in fig. 3b, (XLPE), the structure is non-spherulitic. Fig. 3c shows a distinct impinged spherulitic structure for the 1 wt% TiO₂ doped LDPE.

The d.c. conductivity in polymers has been discussed in terms of models involving charge injection at the electrodes, charge trapping and space charge accumulation in the polymer. The current voltage characteristics on PE films are consistent with space charge limited conduction in this material [1]. It was also recognized that the chemical composition, crystallinity and the morphological structure of the polymer may have a significant effect on its d.c. conductivity characteristics [1, 3]. However, space charge in PE is closely connected to the nature of carrier traps, which in turn, is related to the chemical and structural properties of the polymer. Moreover, the change of crystallinity and morphology leads to changes of the energies, densities and distributions of trap levels and hence resulting in changing the flowing d.c. current in the material.

In LDPE, where spherulitic structure is typical, charge carriers, responsible for its electrical conductivity are usually ascribed to the impure imperfect nature of the spherulite boundaries. Moreover, it was reported by several authors, that the spherulite size is a detrimental factor for the electrical properties of the material [1, 2]. The morphology as well as the chemical composition of XLPE are different from LDPE. Spherulites are not formed in XLPE, where, ideally, all polymer molecules should be a part of a network, and the impure material, responsible for conductivity in LDPE, is most likely to be a part of the crosslinked network in XLPE and cannot migrate [8]. In that case, deeper trapping is expected in XLPE, yielding lower conductivity and higher activation energy. This picture seems to coincide with the present results.

As for the 1wt% TiO₂ doped LDPE, TiO₂ is considered as an n-type excess metal semiconductor, and its addition to the LDPE may result in the modification of the trapping sites in the doped material and hence its conductivity and activation energy. The influence of TiO₂ on the morphology of the doped material and hence on its d.c. conductivity cannot be excluded. The present SEM micrographs show that the spherulitic structure of the TiO₂ doped LDPE is different from that of the plain LDPE.

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REFERENCES


