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Transient charging currents in annealed bulk polyethylene

M. AGUILAR, F. JAQUE
Departamento de Optica y Estructura de la Materia, Universidad Autónoma de Madrid, Cantoblanco, Spain
F. J. BALTÁ CALLEJA, J. PLANS
Instituto de Estructura de la Materia, Madrid 6, Spain

Transient charging currents resulting from the application of a low constant voltage, up to 2×10^4 V cm^{-1}, are investigated in melt crystallized samples of high density polyethylene. Three distinct regions can be clearly distinguished in the current–field characteristic curves at a given time after application of a voltage: (a) a linear region at a low electric field, (b) a negative resistance region in which the slope is negative at a medium electric field, (c) a superlinear region at a high electric field. At low electric fields and for charging times less than 10^3 sec the law of dielectric response, $I \sim t^{-n}$, is obeyed. It is shown that the type of cooling process, after annealing at temperatures near 75° C, markedly influences the current decay. Annealing at this temperature is associated with a partial rearrangement of the lamellar microstructure. The current is enhanced after quenching while it decreases after slow cooling. Various mechanisms to explain the obtained data are considered.

1. Introduction

The d.c. electrical conductivity behaviour of commercial polyethylene (PE), especially at very high electric fields ($> 10^4$ V cm^{-1}) has been reported by several authors [1–4]. These studies are of major interest not only from a technological viewpoint since PE is a good insulator used in electronics having very low dielectric losses, but also, because they permit a new insight into the control of the structure and properties of the material. Although interpretation of the conductivity behaviour of polymers is rather complicated [5] it has long been recognized that the transient current observed is very likely the result of the superposition of different mechanisms acting simultaneously [4].

Fortunately one of these mechanisms may predominate over the others for a specific time range. This is indeed the case for the quasistationary state of the time independent current occurring at very long charging times [3, 6]. The current behaviour here is often attributed to the transport of charged carriers through the sample, because dipole motions are considered to be exhausted. In polymers such as PE the intrinsic thermal carrier generation is admittedly negligible [5]. Hence, the external injection of carriers is often considered necessary to aid in explaining the origin of the carriers and other related conductivity effects [5, 7]. Carrier injection can be interpreted either in terms of a Richardson–Schotky emission [4] or according to a space charge limited current (SCLC) concept [8]. To interpret the anomalous transport properties in semicrystalline materials it is convenient to consider a distribution of localized states (traps) across the band-gap [9, 10]. It has been proposed that traps in polymers originate in the "amorphous" interphase between adjacent crystallites or that they are due to the presence of catalyst impurities or chemical defects within the molecular chains [10]. The carriers are expected to move in this case by a co-operative hopping process between trapping sites. A modified band model with traps delaying the arrival of carriers to the collecting electrode has been shown to be an acceptable alternative to the hopping concept

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[11]. The existence of charged traps such as Poole–Frenkel donors gives rise to a square-root field dependence for the log current, as observed in some d.c. measurements [2, 3].

Let us next consider the transient decay process. For short times, after application of a given voltage, polar materials yield strong polarization currents. Dielectric relaxation processes, ascribed to non-polar polymers, have also been proposed by some authors [12–14]. It is, thus, in this range rather difficult to decide between the two types of contributions: polarization or transport of injected carriers. At high electric fields carrier injection in PE is a well accepted mechanism and the decay current seems to be mainly controlled by the rate of carriers trapped within the sample [2, 15]. At low electric fields, some oxidized (carbonyl) groups, branches, impurities, etc., might contribute to polarization currents overlapping with the transport due to a weak injection from the deposited electrode [3].

The purpose of the present work is to supplement some of the above mentioned studies by examining the conductivity behaviour of melt crystallized PE especially at relatively low electric fields ($< 10^4$ V cm^{-1}). The major purpose of this work is to report on the influence of annealing treatments and subsequent cooling processes on the measured current.

2. Experimental procedure

Samples of high density, linear, PE, Lupolen 5011-K and Marlex 6015 were investigated. The former were measured after cutting the bulk sample into plates 1 to 2 mm thick. The latter were prepared as 200 to 500 μm thick films, about 2 cm in diameter by cooling the polymer from the melt between two glass plates at room temperature. Measurements of conductivity were performed in a cryostat evacuated to 10^{-3} Torr. Electric measurements were made using a thin-walled spring-loaded contact and gold evaporated electrodes on both faces of the sample. This type of specimen and electrode arrangement made the surface path greater than the thickness so that the surface contribution to the total conduction was considerably reduced. Two thermocouples and a programmed controller were used for measurements and control of the temperature. The current produced when the electric field was applied was measured with a Cary-401 vibrating Reed Electrometer. In order to obtain time constants less than 1 sec, the current measurements were carried out with the preamplifier of the electrometer in the "dumping-on" position. Under these conditions the noise level is about 2×10^{-16} amp. The d.c. electrical properties of the specimens in applied fields up to about 2×10^4 V cm^{-1} were measured over the temperature range 21.5 to 30° C.

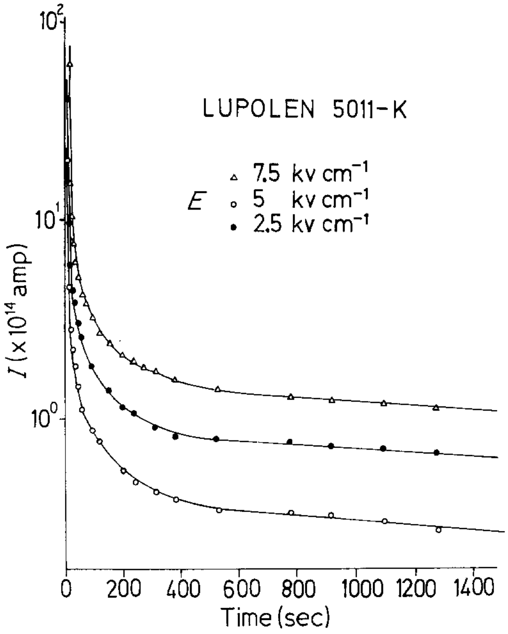

Figure 1 Transient charging currents at various fields for a bulk polyethylene sample measured at room temperature.

3. Results

3.1. Current behaviour for untreated melt crystallized PE

The transient charging currents obtained for PE-Lupolen 5011-K under different applied fields at room temperature are shown in Fig. 1. Similar behaviour as a function of electric field was obtained for Marlex 6015. At any given electric field and temperature the time dependence of the charging current follows the law of dielectric response, $I(t) \sim t^{-n}$, for $t < 10^3$ sec. Fig. 2 illustrates, for a constant field, $E = 7.5 \times 10^3$ V cm^{-1}, and several temperatures, the linear increase of the logarithm of the integral value of the current (polarization), $P = \int_0^t I(t')\mathrm{d}t' \sim t^{1-n}$, as a function of log t. The increase of exponent $(1-n)$ with temperature could be a consequence of a distribution in activation energies, probably corresponding, as we shall comment below, to a dipole mechanism. From the Arrhenius plot of log I against $1/kT$ (Fig. 3) for $t = 3600$ sec and $E =$

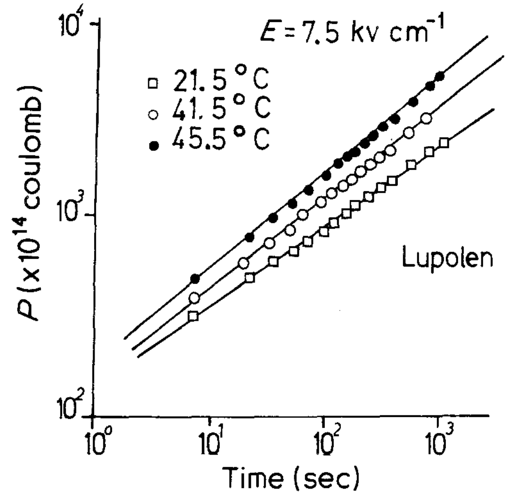

Figure 2 Polarization as a function of charging time at a given field E and different temperatures.

7.5×10^3 V cm^{-1} an activation energy of 0.68 eV is obtained. At shorter charging times lower activation energies are operative, as would be expected from an energy distribution. The exponent n is observed to be field independent although it is weakly temperature dependent.

The characteristic I against E curves obtained after charging times of $t = 30$ and $t = 60$ sec for Marlex 6015 and at $t = 60$ sec for Lupolen 5011-K are depicted in Fig. 4. These data were generated after plotting firstly the corresponding I against t curve for each E value (as in Fig. 1), with sample discharges of several minutes (till this discharge current approaches zero) between each I against t run. The current for a given charging time was then plotted against the electric field applied. E was progressively increased after each I against t run using the same sample. In Fig. 4 three distinct regions can clearly be distinguished: (1) a linear region at sufficiently low fields (2) a relative maximum of current at a value that we shall call E_M, followed by a short decay of negative resistance and (3) a superlinear region at $E > E_M$ for which $I - E^m$, with $m > 1$. This conspicuous behaviour which has not yet been fully recognized in the literature and is common to all times investigated is of particular interest. Such behaviour, although masked by the nature of the log I against $E^{1/2}$ plots, can indeed be recognized through the data of Johnsen and Weber [2, 3] and Röhl and Fischer [4]. At low electric fields ($E < E_M$), the steady state has not been reached even for very long times. In spite of this, linearity below E_M has been established at $t = 1300$ sec. This behaviour neither corresponds to a Pool–Frenkel or Richardson–Schotky mechanism where a log I–$E^{1/2}$ law would be expected, nor to SCLC slopes ($m > 1$). Previous experiments [3] confirmed the same type of linearity at low fields (for 28 h). Finally it is also clear that the position of the peak, suggesting the onset of a new mechanism, remains nearly unchanged, around E_M, with increasing time.

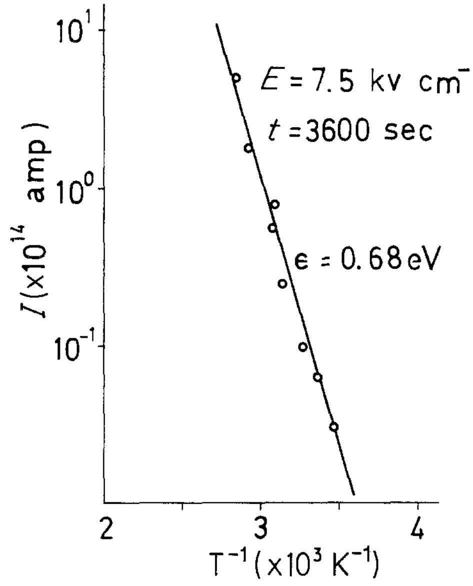

Figure 3 Arrhenius plot of log current against reciprocal of temperature for a PE Lupolen 5011-K bulk sample. The activation energy was obtained at a given field $E = 7.5$ KV cm^{-1} and at $t = 3600$ sec.

3.2. Influence of annealing and cooling-rate on the current behaviour

To obtain more information on the origin of the conduction events in PE the melt crystallized samples were annealed at 76° C for 120 min. The material was then either, (a) quenched at room temperature or (b) very slowly cooled, at a rate of 0.5° C min^{-1} down to room temperature (20° C). Fig. 5 illustrates the strong influence of the annealing treatment and subsequent cooling process on the current behaviour for the bulk Lupolen sample. The current data for the untreated material are shown as open symbols. Both the exponent $1 - n$ and the factor A of the polarization, $P = A t^{1-n}$, increase after quenching (solid cirlces) and decrease after slow cooling (open squares). Fig. 6 shows, in addition, the influence of the annealing temperature, for the slow cooling process, on the three characteristic regions of the

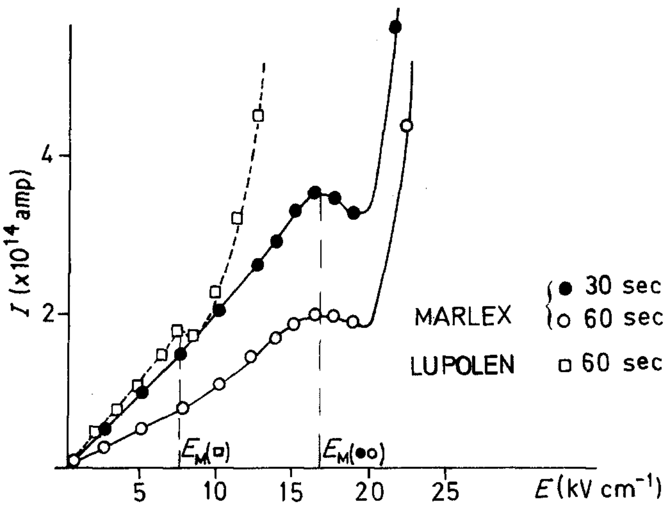

Figure 4 Typical characteristic curves I against E for Marlex 6015 and Lupolen 5011-K measured at 20° C.

I against E plot. Here the shift in the position of the peak current is noteworthy. E_M becomes larger at higher annealing temperatures.

4. Discussion

A look at the three regions of the characteristic I against E curves (Fig. 4) suggests the occurrence of different conduction phenomena depending on E:

The low electric field ($E < E_M$) current behaviour, shows a linear character in favour of a polarization process [16]. In the case of PE, oxidized groups, mainly carbonyl, are admittedly the major source of dipoles [17]. Although infra-red spectra of our samples do not show any absorption band near 1770 cm^{-1}, associated with the carbonyl group, the weak polarization currents measured could be presumably due to a small proportion ($\lesssim$ 10 ppm) of these groups which are optically undetectable. The foregoing results (Fig. 5) hint, in addition, to a certain rearrangement of the PE lamellar microstructure after annealing, giving rise maybe to a redistribution of dipoles between crystalline and non-crystalline regions. Recent small-angle X-ray diffraction experiments on melt crystallized PE [18] indicate, in fact, that after annealing, stacks of thinner lamellae of a double lammelar population selectively melt near 75° C. Recrystallization takes place below this temperature. It would, thus, be reasonable to consider that this selective "melting" and subsequent rate of crystallization of the thinner lamellae has a certain degree of influence on the kinetics of the current. One could, hence, attempt to relate the quenching of the melted lamellae (giving rise to a more imperfect surface layer and to an increase in the number of free dipoles in the non-crystalline regions) to the observed enhancement of the polarization current. The current decrease observed when cooling slowly, could be consistent, according to this view, with a better crystallized lamellar structure having a larger number of dipoles which are trapped within the lattice. At low electric fields, we are, hence, rather inclined to think in terms of a prevailing internal dipole polarization mechanism. However, the possibility of a weak carrier injection

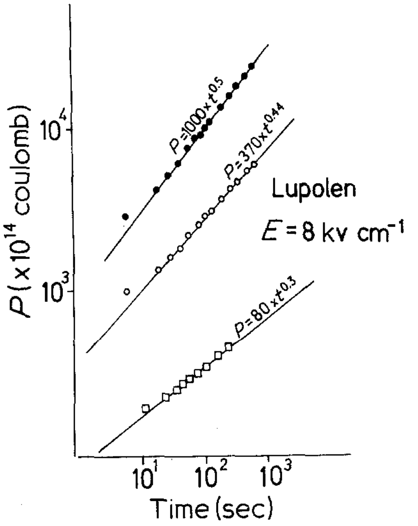

Figure 5 Polarization, P, as a function of time at a given field $E = 8$ KV cm^{-1} for: (a) an untreated PE sample (open circles); (b) after annealing at 76° C for 100 min and subsequent quenching at 20° C (solid circles); (c) after annealing, as in (b) and slowly cooling at 0.4° C min^{-1} (open squares).

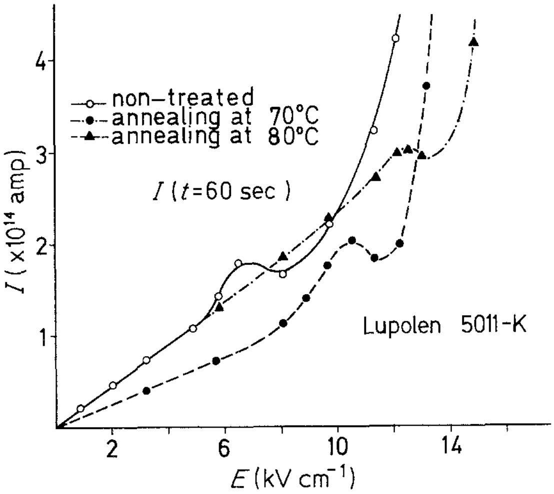

Figure 6 Characteristic curves I against E for an untreated PE sample, and after annealing it at 70 and 80°C, respectively, with a subseqeunt cooling rate of 0.4°C min^{-1}.

contribution which could predominate near and above E_{M} is not discarded.

The characteristic curve region having a negative slope ($E \sim E_{\mathrm{M}}$) resembles the curves reported for tunnelling through a thin layer of PE single crystals [19]. The great thickness of our samples makes it difficult here, however, to think in terms of such a mechanism. Space charge limited currents reportedly, furnish, instead, a plausible alternative explanation for the negative resistance region [20].

At high electric fields ($E > E_{\mathrm{M}}$) carrier injection is probably contributing to SCLC and/or Poole–Frenkel currents. The superlinear region for $t = 1300$ sec corresponding to $I \sim E^m$ yields values, $1 < m \lesssim 2$ which would support the SCLC current concept [8]. High electric fields facilitate, on the other hand, injection by reducing the potential barrier between the electrode and the sample. In addition, injection is also favoured by the existence of surface states which can take up a charge directly from the metal surface [8]. It is very tempting to think that the current peaks at E_{M} showing negative slopes are related to the onset of injection. Thermal treatment would, consequently, be able to modify also the structure of the surface traps and, as a result, lead to the observed shift of the E_{M} maxima to higher electric fields with increasing annealing temperature, after slow cooling.

5. Conclusions

In conclusion, the present study presents new aspects of the conductivity phenomena occurring in polyethylene, highlighting the relevance of annealing treatments at moderate temperatures (70 to 80° C). In particular, the current variations detected appear to depend markedly on the rate of cooling of the polymer after the annealing process. The latter cooling rate is correlated to the varying state of order of the lamellar microstructure, which in turn, probably influences the distribution of dipoles between ordered and disordered regions of the polymer.

References

1. G. STETTER, *Kolloid ZuZ Polymere* **215** (1967) 112.
2. U. JOHNSEN and G. WEBER, *Colloid Polymer Sci.* **252** (1974) 836.
3. *Idem, Progr. Colloid and Polymer Sci.* **64** (1978) 174.
4. P. RÖHL and P. FISCHER, *Kolloid ZuZ Polymere* **251** (1973) 997.
5. M. KRYSZEWSKI, *J. Polymer Sci.* **C50** (1975) 359.
6. J. M. VAQUERO and F. J. BALTÁ CALLEJA, *Colloid Polymer Sci.* **255** (1977) 967.
7. M. A. LAMPERT and P. MARK, "Current injection in Solids" (Academic Press, New York, 1970).
8. M. KRYSZEWSKI and SZYMANSKI, *J. Polymer Sci.* **D4** (1970) 245.
9. N. F. MOTT and E. A. DAVIS, "Electronic Processes in Non-Crystalline Materials", (Clarendon Press, Oxford, 1971).
10. H. BAUSER, *Kunststoffe* **62** (1972) 192.
11. F. W. SCHMIDLIN, *Phys. Rev.* **B16** (1977) 2362.
12. P. FISCHER and P. RÖHL, *Kolloid ZuZ Polymere* **251** (1973) 941.
13. V. ADAMEC, *J. Polymer Sci.* **A2**,**6** (1968) 1241.
14. V. ADAMEC, *Kolloid ZuZ Polymere* **237** (1970) 219.
15. O. DEHOUST, *ibid.* **235** (1969) 1271.
16. K. W. WAGNER, *Ann. Physik* **40** (1913) 817.
17. P. HEDVIG, "Dielectric Spectroscopy of Polymers" edited by A. Hilger (Adam Hilger Ltd, Bristol, 1977).
18. J. MARTINEZ SALAZAR and F. J. BALTÁ CALLEJA, *Polymer Bull.* **3** (1980) 7.
19. A. VAN ROGGEN, *Phys. Rev. Lett.* **9** (1962) 368.
20. T. W. HICKMETT, *Bull. Ann. Phys. Soc.* **7** (1962) 179.

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