High mobility conduction in insulating polymers through fast soliton-like charge pulses

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Abstract. We present evidence for the existence of a new form of charge transport in insulating polymers which takes the form of charge pulses that move exceptionally quickly across the insulation in comparison to the charge carrier mobility typical of such materials. This phenomenon could be associated with electromechanical compression of the polymer (a minimum amount of charge is needed for this to occur) that triggers a discontinuous injection of charge at the electrodes and allows transport inside the bulk through chain displacement modes. These pulses behave as charged solitary waves, or solitons, with a speed that corresponds to a mobility of some orders of magnitude higher than that of independent carriers.

1. Introduction

Literature indicates that insulating polymers exhibit generally very low electrical conductivity and the mobility of the charge carriers is low even at high fields (e.g. $10^{-16}$ - $10^{-14}$ m²V⁻¹s⁻¹ compared to $> 10^{-5}$ m²V⁻¹s⁻¹ for semiconductors and metals) [1-3]. In fact, the electrical conductivity is associated not just with the low carrier mobility, but also with the concentration of intrinsic and extrinsic carriers. Up to quite high fields the carrier concentration is mostly determined by extrinsic carriers as the gap between valence and conduction bands is so high that the concentration of intrinsic carriers is essentially non-existent. Extrinsic carriers are contributed by impurities and contaminants, as well as electronic charges (electrons/holes) injected from the electrode/insulation interface. If the electric field is above a certain value (the so-called “threshold for space charge accumulation” [4]), an excess amount of charge is injected in the material, more than can be extracted from the other electrode, thus accumulating in the bulk as space charge. This charge is trapped in localized states of the material and can move from one electrode to the other by hopping between traps [3]. The crucial feature of this ‘traditional’ approach is that the carriers move incoherently as point particles independent of one another and without affecting the potential surface on which they move, i.e. the traps are localised and exist whether or not carriers reside in them. In this approach the current is a continuous flow of carriers, which gradually approaches a steady state value after an electric field is applied to the insulating polymer.

Recent experiments however, show that the current picture is not always adequate [5]. Thanks to ultra-fast space charge acquisition systems, small, but repetitive, charge pulses of both polarities, travelling very fast from anode to cathode and vice-versa, have been observed in polyethylene specimens at moderate fields. The following sections will provide evidences of this new and unexpected conduction mechanism.
2. Experimental setup
The specimens considered in this paper consist of cable models reproducing HV cables on a reduced-scale (mini-cables), made by three layers: inner semicon (0.7 mm thick), insulation layer of cross-linked-polyethylene (XLPE) material (1.5 mm thick) and outer semicon (0.15 mm thick). The conductor diameter is 2.8 mm (Figure 1).

![Figure 1. Sketch of tested minicable. Conductor diameter = 2.8 mm; Inner semicon thickness = 0.7 mm; dielectric (XLPE) thickness = 1.5 mm. Outer semicon = 0.15 mm.](image)

Minicable sections of 1.5 m length were kept at 80°C for 5 days in order to expel volatile by-products produced during the cross-linking of its polyethylene insulation and volatile solvents present in the carbon particle loaded polymer (semicon) that connects the insulating polymer to the metallic electrodes. They were then placed in a controlled temperature environment for the measurement of space charge. This was realised by means of the Pulsed ElectroAcoustic (PEA) technique [6] at field values exceeding the threshold for space charge accumulation, e.g. with average fields of about 40-50 kV/mm (the threshold is around 10 kV/mm at 25 °C). The effect of temperature on charge dynamics was investigated by carrying out tests in an oven under isothermal conditions (no temperature gradient applied to insulation) at 35, 45 and 70 °C.

Space charge profiles were recorded by means of an ultra-fast-acquisition system [5]. The signal to noise ratio is reduced by averaging 100 signals to produce each space charge profile using a digital signal averager that has a fast processor and PC connection. It is therefore able to acquire, average, and store signals at a very high rate (up to 1 MHz). This allows the acquisition and display of space charge profiles every 25ms. The space charge amplitude resolution achieved is about 0.03 C/m³.

3. Experimental results: the existence of fast charge pulses
A sequence of both positive pulses (from the anode) and negative pulses (from the cathode), see Figures 2a and 2b, are observed contemporarily. The pulse amplitude is small (0.07 to 0.15 C/m³) and remains around the same value throughout the measurement of the pulse sequence, which occurs with a repetition rate of 2.5 s⁻¹ for negative pulses and 3.5 s⁻¹ for positive pulses at mean temperature T = 70 °C and average electric field E = 40kV/mm. Each pulse maintains a constant speed and shape during transit, which takes less than 0.5 s at the range of measurement temperatures and fields. In particular, transit times decrease noticeably with temperature increase from 35°C to 70°C, that is about 3 and 6 times for positive and negative pulses.

The measurements also show that extraction is not immediate. A charged region of opposite polarity to that of the extracting electrode (heterocharge), see Figure 3, is built up as incoming pulses reach the electrode region and are delayed in their extraction. Indeed, even if each charge pulse involves only a small amount of charge (about 0.07-0.1 C/m³), the pulses are produced with a high repetition rate and therefore after some seconds from the beginning of polarization, several pulses accumulate a noticeable amount of heterocharge close to both electrodes. This heterocharge build up has been observed in our experiments only when a semiconducting layer is present between insulation and metal (copper or aluminium) electrode and for relatively-thick specimens. Tests performed on thin flat specimens having semicon layer only on one side showed, in fact, that no heterocharge was observed close to the electrode not in contact with the semicon [7]. It seems that semicon material can partially block the extraction of injected charge at the counter electrode allowing, thus, a heterocharge build up close to the partially-blocking electrode [7].
Figure 2. (a) Fast positive charge pulses crossing the insulation, (b) fast negative charge pulses crossing the insulation. The time relevant to each profile acquired is reported in the legend. The arrow indicates the charge pulse direction. Test electric field = 40 kV/mm, temperature = 45°C.

Figure 3. Space charge distribution in the insulation bulk as a function of acquisition time. The colour diagram indicates the accumulated charge amount according to the colour scale reported on the right (cold colours = negative charge, warm colours = positive charge). A heterocharge build up at both electrodes over time is observed. Average field = 50 kV/mm, max polarization time = 40s, temperature = 70°C.

4. Discussion: from charge pulses to solitons

The retention of shape as the pulses cross the sample despite the difference in field between the leading edge and trailing edge (the transit time is too short for carrier diffusion to have an effect) and the lack of acceleration as the counter electrode is approached, implies that such pulses cannot be a cluster of independent carriers. Instead they must be coherent charged entities, i.e. solitons [8, 9]. However the transit time is very fast and our spatial resolution about 40µm, so that we cannot rule out the possibility of a slight redistribution of charge within the pulse; for this reason we have termed the pulse soliton-like [10].

It has to be pointed out that a critical amount of charge, not changing with temperature and field, but depending on the nanofiller concentration, is needed to create a charge soliton. This can be explained by considering the effect of the electromechanical compression at the electrode/insulation interface. An idea to explain soliton injection is displayed in Fig. 4. According to Lewis et al [19] the applied electric field produces a pre-compression of the polymer electrode interface. In addition to this, a given amount of extracharge, ΔQ, which causes an increase of the applied field, ΔE, needs to be available at the electrode/insulation interface in order to produce an extra-compression of the polymer chains against the electrode suitable for the charge ΔQ to tunnel into the chain. After charge injection the interface field and compression drops down, leading the polymer chain to release, thus stopping further charge tunneling. At the end of the process, the charge soliton ΔQ is injected into the material.
It should be observed that this mechanism produces a discontinuous injection of charge pulses, each one having the same size $\Delta Q$. In order to have a repetitive packet injection, in fact, the same critical amount of excess charge at the polymer/electrode interface has to be created to give rise the extra-compression that triggers another packet injection.

$\Delta Q = \text{'critical' charge amount}$

$E = \text{electric field at the electrode/polymer interface}$

$E_a = \text{applied (laplacian) field}$

$\Delta E = E - E_a$

**Figure 4.** Soliton injection mechanism due to electromechanical compression of the polymer/electrode interface.

In order to provide a quantification of the charge dynamics, the average mobility value, $\mu$, of the soliton-like charge pulses (positive and negative) can be obtained roughly from [1]:

$$\mu = \frac{v}{E}$$

where $v$ is the speed of the charge packet and $E$ is the average electric field applied to the insulation.

The field and temperature dependence of the mobility, Figure 5, allow the main features governing transport of the soliton-like charge pulse to be identified, by use of a general expression valid for hopping and tunneling mechanisms [3, 11],

$$\mu(E, T) = \frac{2kTR}{hE} \exp\left(-\frac{\Delta U}{kT}\right) \sinh\left(\frac{eER}{2kT}\right) \exp(-\alpha R)$$

where $R$ is the distance along the field direction the charge carriers in the pulse have to transfer, $k$ the Boltzmann constant, $h$ is Planck’s constant, $\Delta U$ the thermal activation energy to an excited state from which the particle can tunnel [12] into an electronic state on the receiving site with a probability $\exp(-\alpha R)$. The value of the coefficient $\alpha$ is related to the wave function decay and determined by the mass of the tunnelling particle and the barrier through which it tunnels when in the excited state [12].
Figure 5. Arrhenius plot of pulse mobility at two different fields. (a) Positive pulses, (b) negative pulses. The overall activation energy, $E_a$, is also indicated for each field.

In the case of the positive solitons the mobility exhibits an Arrhenius behaviour, i.e. $\mu(E,T)$ is proportional to $\exp(-\Delta U - eER/2kT)$, Figure 5a, with an overall activation energy that is only slightly dependent upon the value of electric field through the term $eER/2kT$ in the exponent. We find that $0.25 \text{ eV} \leq \Delta U \leq 0.33 \text{ eV}$ and $0.05 \text{nm} \leq R \leq 4 \text{nm}$. It has to be noted that the large range of variation for $\Delta U$ and $R$ is due to limits of the experimental accuracy in evaluating the activation energy. The upper bound to $R$ and $\Delta U$ has been calculated by assuming the values of $E_a$ reported in Figure 5a, the lower bound has been estimated considering that the field-dependence of the overall activation energy is zero. The tunneling factor, $\exp(-\alpha R)$, can be calculated consequently by inserting the values of mobilities of Figure 4a, $\Delta U$ and $R$ in the equation (2). It is found that $1 > \exp(-\alpha R) \geq 10^{-3}$.

The field dependence of the overall activation energy of negative soliton mobility is much greater (Figure 5b) and a similar analysis gives $R \approx 14 \text{nm}$, $\Delta U \approx 0.76 \text{eV}$, and $\exp(-\alpha R) \approx 1$, with a larger accuracy.

These results show that the positive solitons move by a thermally activated tunnelling transfer between sites less than a few nanometres apart. This is consistent with carriers that are positive ‘holes’ i.e. electron vacancies in the valence bonds of the polymer [11]. Such species can move easily along straight chain sections, but will be trapped at chain bends, twists, and kinks, and will have to transfer between chains by a reverse tunnelling of electrons. Polyethylene and cross-linked polyethylene are semi-crystalline and in extruded insulation such as that investigated will contain crystalline regions in the form of ribbon-like lamellar plates with amorphous regions sandwiched inbetween [2, 11]. Neighbouring chains are not normally close enough to make tunnelling effective, however the so-called crankshaft (or kink) motions [13], operative only in the amorphous regions, can be expected to bring a small region of different chains close enough to allow tunnelling to occur. The activation energy for such motions [14] lies close to the range of $\Delta U$ found here. This implies that the positive soliton-pulses are holes bound to kink/crank-shaft distortions in the amorphous regions that travel through the polymer as a solitary wave by inter-chain tunnelling transfer enabled by thermally activated crank-shaft/kink displacements.

The value of $\Delta U \sim 0.76 \text{eV}$ obtained for the negative soliton-pulses would usually be associated with intermediate range electron trap depths [11], which are typical of traps at polymer-free volume interface [16]. However, we note that this value is of the magnitude of the activation energy for the $\beta$-motions of the polymer chain [14]. This mode of polymer motion involves whole segments of polymer chain and also operates only in the amorphous part of the polymer. The amorphous regions have a lower density than the polymer crystal and contain potential lattice sites that are unoccupied by atoms of the polymer chain termed free volume. This free volume fluctuates in space and time [17] due to the $\beta$-motion displacements. Electrons in polyethylene will trap in the free volume [16, 17] or on the chain bends at the surface of such regions [18]. We suggest that in a negative soliton-pulse, electrons...
associated with free volume traps drive a field-assisted activation of the $\beta$-motion that opens up the polymer chains that inhibit the free transfer of electrons. The electron and the associated free volume are carried together through the amorphous regions as a single entity, a little like the flexing of capillary walls moves blood along in the body. Thus in both cases the soliton-pulses are a quickly moving charged solitary wave in the amorphous region, with the positive and negative soliton-pulses differing in the type of polymer displacement mode with which the charge is bound.

5. Conclusions
Experiments show the existence a new conduction mechanism, i.e. a small amount of charge moves in the amorphous region as solitons, even if the largest concentration of injected charge carriers follows the conventional pattern. The solitary wave nature of the pulse means that there is no inter-change of charge between the two transport systems, which act as effectively independent transport sub-systems. As a consequence, the fast pulsive packets persist into the steady state regime, where they are superimposed on the steady state current as noise fluctuations, small to detect. The fast pulses however dominate in the transient regime. Their build up of heterocharge at the electrode interfaces, which increase the interface fields, may affect negatively insulation system reliability during service.

6. References
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