

# Discovery of an unknown conduction mechanism in insulating polymers

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**Abstract:** Polymer dielectrics are widely used in electrical and electronic apparatus and devices because of their capability to insulate conductors, withstand high fields and suffer negligible conductive losses. Their near-to-zero conductivity has been explained in terms of long-accepted theories of electronic and ionic transport that lead to the accumulation of local net charge regions at high electric fields. Here the authors describe a previously unknown conduction mechanism consisting of small bipolar ultra-fast charge pulses crossing the polymer with the mobility, as large as, 4 to 5 orders of magnitude greater than that of the previously known. The authors show that this motion is a consequence of molecular relaxation processes triggered by the electric field locally enhanced by the pulses themselves. Pulse accumulation at the electrodes increases interface field and thus contributes substantially towards premature failure in insulating dielectrics in DC fields.

## 1 Introduction

Models describing the conduction mechanisms in insulating dielectrics have been well known for decades, and are based on injection/extraction of electrons from electrodes and hopping between localised states or traps, and the diffusion of ionic species [1]. Over the years it has become evident that the injection/hopping mechanism proposed by Mott and Gurney and reviewed in [2], held mostly at low electrical fields. At higher fields space charge could be accumulated within a dielectric residing in physical or chemical traps, thus altering the local electric field and changing the conduction current [2]. The advent of direct space charge scoping techniques, such as laser impulse modulation or pulse electroacoustic (PEA), [3], has provided direct evidence of the space charge accumulation within the insulating polymer, and the relevant Poisson electric field modification proposed. In addition to the above-mentioned mechanisms for incoherent charge carrier transport and space charge accumulation, it was found that at high fields ( $\geq 90$  MV/m) injected charge could transit the dielectric in the form of repetitive packets [4], usually of one polarity, which is shown by monitoring of space charge during accelerated life tests, to bring about the rapid breakdown. The mobility of these packets ( $10^{-16}$ – $10^{-14}$  m<sup>2</sup>/Vs) was found to be of similar in magnitude with that of incoherent carrier transport by trap-to-trap hopping and their formation and transport have been explained in terms of well-known physical processes such as a moving ionisation front or, in different conditions, negative differential resistance, see [4]. An unexpected outcome of experiments carried out through enhanced (very fast acquisition times and large bandwidth) PEA systems, however, was the observation of repetitive small charge pulses of both polarity, produced at lower fields (20–50 MV/m) but having a mobility of 4–5 orders of magnitude higher than those formed at the higher fields. This is a counter-intuitive behaviour, as charge carrier mobility would be expected to decrease (or at least remain the same) when the field is reduced, which implies that an unknown transport mechanism is involved. Here we present the experimental evidence for the existence of these pulses and explain their formation and transport in terms of the mechanical deformation produced by the electric field of the pulse itself in flexible polymeric dielectrics [5]. Their existence has implications for the use of such polymers to insulate DC systems since they produce a rapid step-wise build-up of space charge at the electrodes

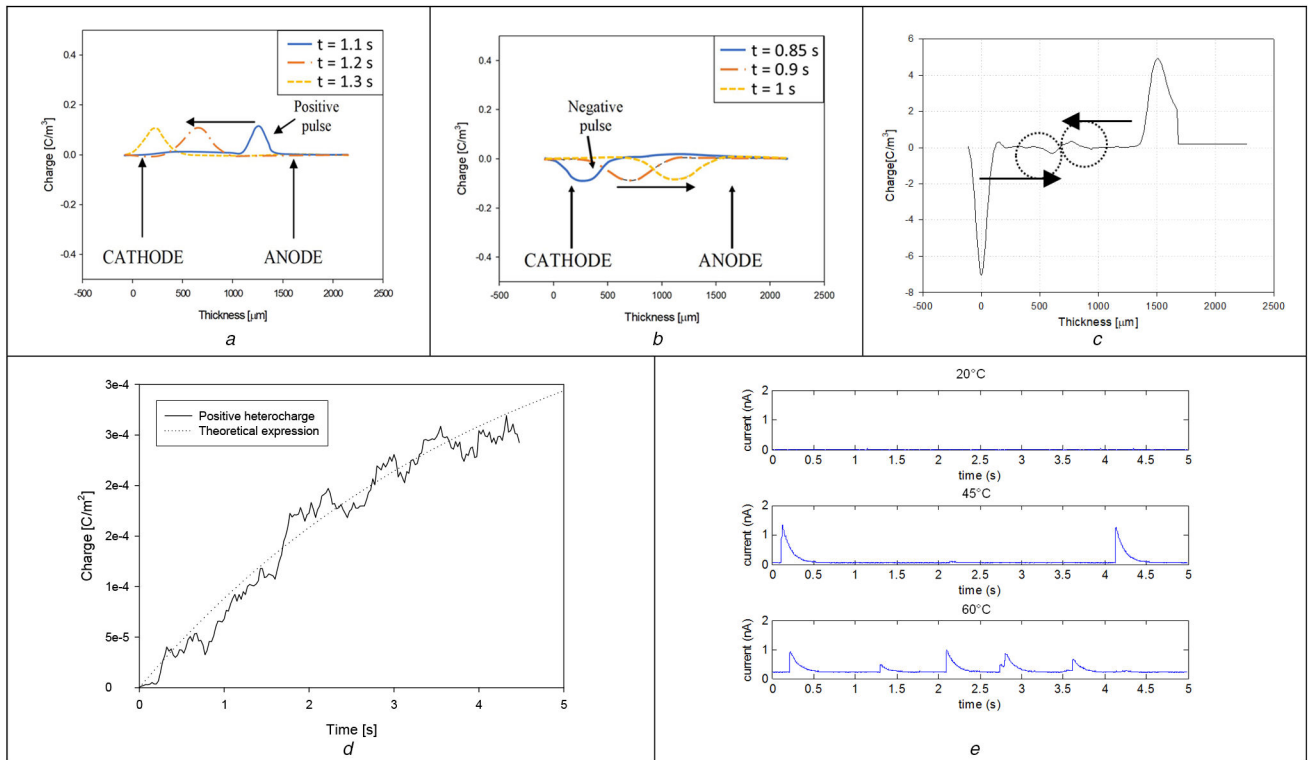
under typical design fields and temperatures that enhances the electrode field and promotes rapid breakdown.

## 2 Evidence for fast pulses

We have detected ultra-fast pulses in a number of polymeric insulating materials with both very different chemical composition and material morphology, see [6, 7] and references therein. These range from the rubbery semi-crystalline cross-linked polyethylene (XLPE) composed solely of C-C and C-H bonds to unfilled and filled network epoxy resins that contain aromatic rings and nitrogen atoms and have various degrees of mechanical flexibility depending upon their composition, temperature, and the presence or otherwise of nano-silica fillers. The fast pulse phenomenon in insulating polymers, therefore, does not require a specific chemical formulation or morphology for its occurrence.

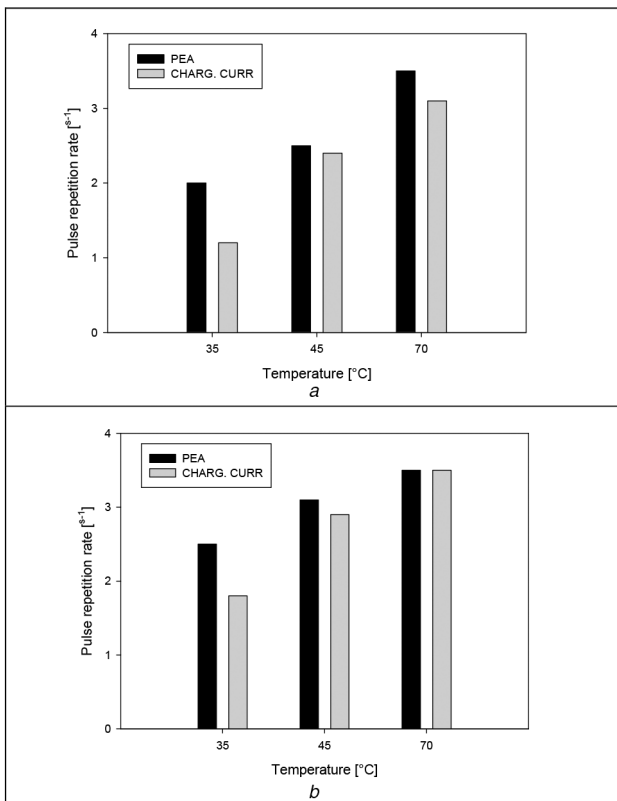
### 2.1 Experimental procedures

The space charge pulses were observed and measured using an enhanced PEA measurement system [8]. Model cables with 1.5 mm thickness of XLPE were used for the investigation of XLPE with DC electric fields ranged between 20 and 40 kV/mm and temperatures from 20 to 70°C. The moulded flat specimens, 0.5–1 mm thick, were used for measurements in the epoxy resins. In order to obtain a good enough signal to noise ratio such that measurement of the space charge distribution within the sample can be made with sufficient time resolution that the pulses can be identified and their movement followed, a 12 bit digital signal averager capable of acquiring, averaging and storing signals at a rate up to 250 MHz was used to collect the large number of response signals required. The electrical pulse originating the pressure waves had a fixed amplitude and repetition rate of 500 V and 2 kHz and a duration of 10 ns. The spatial resolution is determined by this duration and the thickness of the piezoelectric element being used. On the other hand, the sensitivity is determined by the quantisation level of the digital acquisition system being used, the pulse amplitude and the piezoelectric constant of the sensitive element. For this work, an overall spatial resolution of the system of 10  $\mu$ m was reached, with a sensitivity of 0.05 C/m<sup>3</sup>. Wavelet transforms were used for further signal enhancement.



**Fig. 1** Measurement on XLPE (1.5 mm thick) insulated model cables: *a–d* time-dependent space charge distributions (Laplacian DC poling field on the conductor 30 kV/mm, temperature  $T = 45^\circ\text{C}$ )

(a) Motion of positive pulse, (b) Motion of negative pulse, (c) Positive and negative pulses moving through one another, (d) Time-dependent accumulation of positive pulse charge at the cathode, (e) Examples of pulses in the DC charging current corresponding to the detected internal space charge pulses (at applied field 30 kV/mm, temperatures as marked)



**Fig. 2** Comparison of repetition rate of ultra-fast charge pulses detected during charging current measurements and space charge measurements in XLPE cable models, 30 kV/mm

(a) Positive pulses, (b) Negative pulses

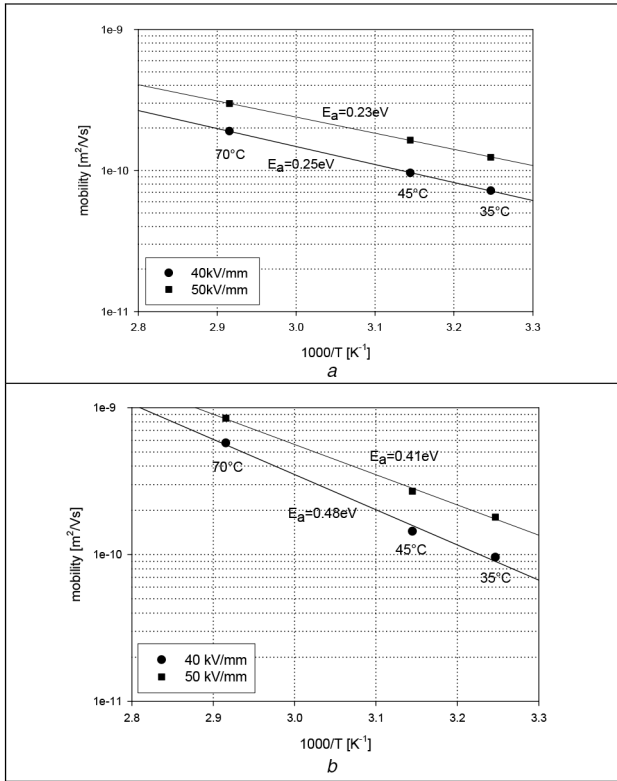
The current pulses were obtained from measurements of the DC charging current in the external circuit at the same time as the space charge pulses were measured in the bulk material using an

electrometer with a  $5\ \mu\text{s}$  integration time, and a sampling rate of 2 kHz. A high-pass filter with a cut-off frequency of 100 Hz ( $-3\ \text{dB}$ ) was connected to the input of the waveform analyser. This was done to remove the low-frequency components of the detected current, associated with conduction and polarisation processes. Since the bandwidth of the pico-ammeter (100 kHz) limits the frequency spectrum of the pulse, this measuring technique should be considered mostly as a peak detector.

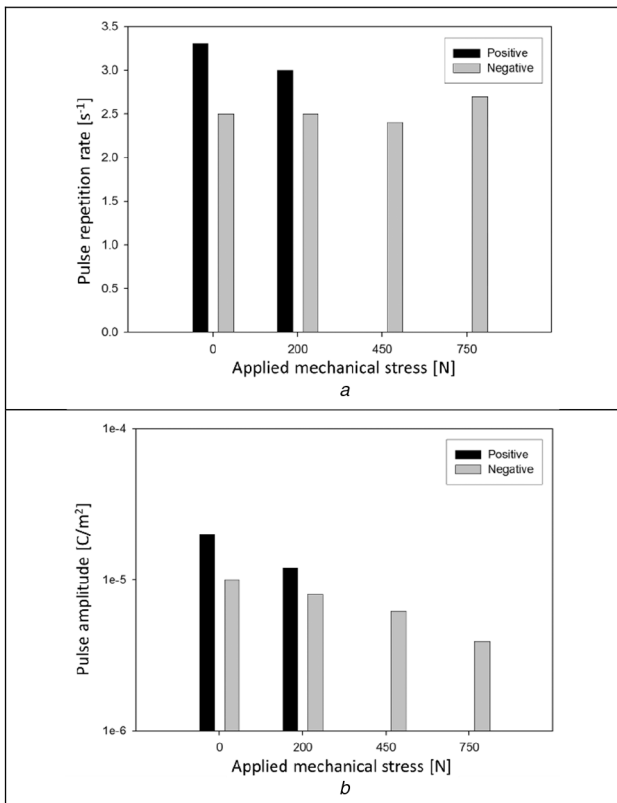
## 2.2 Fast pulse measurement results

Examples of the charge pulses detected in XLPE insulated model cables are shown in Fig. 1a (positive pulses) and Fig. 1b (negative pulses) as a function of time during transit of the insulation. These charge pulses cross the insulation with a mean mobility (calculated as mean pulse speed divided by mean electric field) of  $\sim 10^{-10}$  and  $\sim 2 \times 10^{-10}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}$  for positive and negative pulses, respectively. Such values are four orders of magnitude larger than the typical known values for charge carrier mobility in XLPE [1, 9]. There is no apparent attenuation or dispersion during the transit, and in instances where both polarity pulses are present at the same time move through one another without loss of identity, Fig. 1c. The repetition rate of the fast charge pulses is  $1\text{--}4\ \text{s}^{-1}$  depending on temperature and field, thus very low, indicating a strong influence from the electrode/polymer interface in their generation. The pulses are not extracted immediately upon reaching their counter electrode, instead a delay in extraction results in a step-wise build-up of space charge with the opposite polarity to that of the electrode, an example of which is shown in Fig. 1d. The presence of these fast charge pulses has been confirmed independently of the space charge measuring technique (PEA) by directly measuring the DC charging current of the XLPE model cables in the same range of fields and temperatures. Using a fast sampling rate, a sequence of small current pulses was detected, Fig. 1e, at time intervals that correspond to those of the fast charge pulses, Fig. 2, with the negative pulses producing the smaller current pulses in accordance with their smaller magnitude.

Arrhenius plots of the space charge pulse mobility show that it is a thermally activated mechanism. The example shown in Fig. 3



**Fig. 3** Arrhenius plots for pulse mobility in XLPE model cables, with poling fields of 40 and 50 kV/mm  
(a) Positive pulses, (b) Negative pulses



**Fig. 4** Fast pulse measurements on XLPE insulated cable models under static mechanical stress  
(a) Pulse repetition rate, and (b) Amplitude of pulse charge density integrated over the measured pulse length

is for the XLPE-insulated model cables where activation energies of 0.23–0.25 eV were found for positive pulses and 0.41–0.45 eV for negative pulses with a limited, if not negligible, dependence on

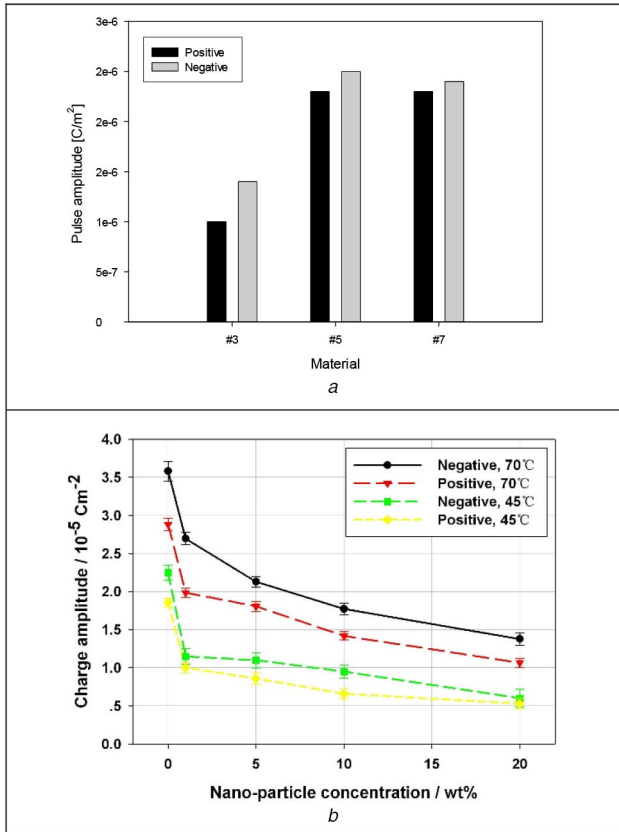
applied field. These values are very much smaller than those reported for the charge carrier mobility in XLPE (see [7–10] and references therein), which are typically 1 eV or greater corresponding to the deep traps that control charge carrier transport on a macroscopic scale as found for other forms of carrier transport including the larger charge packets formed at higher fields. The implication is that when the charge carriers take the form of a fast space charge pulse, they are able to move without having to be activated from a deep trap to the mobility state.

The values obtained for the activation energy of the mobility of the positive and negative pulses in the XLPE insulated model cables are close to those of the  $\gamma$  and  $\beta$  mechanical relaxations in XLPE, see [10], and references therein. This raises the possibility that local chain rearrangements associated with these relaxations are involved in the pulse transport. We therefore, performed space charge measurements on the model cables simultaneously with a longitudinal static mechanical stress applied to the conductor, which corresponds to compressive stress on the insulation. This has the effect of making the polymer morphology stiffer and restricting the ability of the polymer chains to become involved in relaxation motions, and so should influence the formation and transport of fast charge pulses if mechanical relaxation motions are a feature of the phenomena. The result is displayed in Fig. 4, where it can be seen that the pulse amplitude decreases on increasing the mechanical stress, till both positive and negative pulses disappear, while their mobility,  $\mu$ , slightly increases. It therefore seems clear that chain relaxation displacements are involved in fast pulse formation. The influence of mechanical stress upon the pulse mobility was assessed using [11]

$$\mu = \mu_0 \exp\left(-\frac{\Delta}{kT}\right) \exp\left(\frac{\Delta V p}{kT}\right) \quad (1)$$

Here,  $\mu_0$  = model constant,  $\Delta$  = thermal activation energy,  $p$  = compression stress (in  $\text{N/m}^2$ ),  $T$  the absolute temperature in Kelvin,  $k$  the Boltzmann constant, and  $\Delta V$  = stress activation volume. The value of  $\Delta V$  for the positive pulses was found to be  $0.09 \text{ nm}^3$ , which is near to its value for the  $\gamma$  mechanical relaxation of un-XLPE (under compression) reported to be in the range of  $0.02$ – $0.03 \text{ (nm)}^3$ , and likely larger for XLPE [12]. This supports the association of the positive pulse transport with the  $\gamma$  mechanical relaxation. In the case of negative pulses  $\Delta V = 0.18 \text{ nm}^3$ . No data relevant to the  $\beta$  relaxation has been found, but since this relaxation involves much larger chain segments than the  $\gamma$  relaxation [13], it is likely that its  $\Delta V$  will be much larger and consistent with associating the negative pulses with the  $\beta$  relaxation. The repetition rate (Fig. 4a) is determined by the rate of recovery of the conditions required for tunnelling injection of carriers at the electrode once the previous pulse has moved into the polymer. The injection of negative carriers takes place directly into the amorphous regions of XLPE which are easily compressible it is likely that the recovery rate and, hence, repetition rate for negative carriers will not be much changed by the macroscopic compression. On the other hand the injection of positive carriers (i.e. holes) will take place into lamella chains before their rapid transit to the amorphous/lamella interface [14]. In this case it is possible that the recovery of a suitable compressed state will take longer as the macroscopic compression increases because it requires a reordering of the lamella arrangement.

The relationship between fast pulses and polymer mechanical properties was investigated further through experiments carried out on epoxy resins that had their rheological and mechanical properties altered in a defined way by, adding plasticisers, and/or adding boehmite and silica ( $\text{SiO}_2$ ) nanofillers in different concentrations. No fast pulses were detected when the epoxy was in its glass state at the observation temperature. When, however, the epoxy was made flexible due to the addition of nano-particles and/or flexibiliser fast pulses were detected whose pulse-charge amplitude, repetition rate and mobility increased as Young's modulus decreased, Fig. 5a. In the case where the base epoxy resin is flexible at the observation temperature fast pulses were detected, but the addition of nano-particles increased Young's modulus and



**Fig. 5** Charge pulse amplitude for two types of epoxy base materials filled by nanoparticles

(a) Base epoxy in glass state. Increasing boehmite nanofiller concentration, 3 wt% (#3), 5 wt% (#5), 7 wt% (#7), progressively reduces Young modulus (lowers glass transition temperature  $T_g$ ), (b) Base epoxy is flexible. Increasing silica (SiO<sub>2</sub>) nanofiller concentration increases Young modulus (increases  $T_g$ )

reduced the pulse-charge amplitude, repetition rate and mobility, Fig. 5b. Pulse mobility is in the range of  $10^{-9}$ – $10^{-10}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> depending on the type of base material, nanofiller concentration and temperature, going from materials with lower Young modulus to those having higher modulus (which show values near to those detected for XLPE). While the pulse magnitude varies considerably with the material and mechanical stress, being largest in those materials that exhibit the biggest mechanical response, the total charge per pulse (calculated by integrating the charge density over the pulse and multiplying by the area of the piezoelectric detector over which the measured signal is averaged) is almost constant as a function of electrical poling field, and only slightly variable with temperature. These features suggest that the pulse is a kind of quantum of charge whose amount is determined by the mechanical response of the material, and is largest in the most flexible of the materials studied. In XLPE the positive pulse charge is about  $3 \times 10^{-9}$  C (i.e.  $\approx 2 \times 10^{10}$  electrons) about twice the charge of the negative pulse. If the pulse can be thought of in this way then the repetition rate, varying from  $\sim 1$  s<sup>-1</sup> to  $\sim 10$  s<sup>-1</sup>, would be controlled by the time taken to build-up the required amount of charge.

### 3 Pulse formation and transport

The observation that the fast charge pulses retain coherence and pass through one another unchanged during transit means that their motion cannot be described by the incoherent trap to trap transfer of the charges of which they are composed [13]. Instead, their propagation has the features of a charged solitary wave, i.e. they behave as solitons [10, 15]. Theory of their formation, therefore, needs to address a number of points, namely the reason for their formation as pulses, their coherent transport and its high speed, and the involvement of material flexibility via the mechanical relaxations.

The basic physical concepts involved can be deduced by examining the charge carriers and mechanical relaxations that occur in XLPE. Here negative carriers are electrons that reside outside but alongside the polyethylene chains ([16, 17] and references therein). Positive carriers are ‘holes’, i.e. a C-C bond with an electron removed [14, 18, 19]. Holes and electrons move in different ways; the electron as a particle translating from trap to trap via the space between the polymer chains and the hole by reverse electron tunnelling between neighbouring chains [20]. In both cases, the traps are located in the amorphous/crystalline lamella interface where the regular arrangement of the chains in the lamella is lost. The charge on the carrier polarises the XLPE and displaces the chains in its vicinity, [14, 21], so that in order to move as an independent particle, energy of the order of 1 eV must be provided. This energy can release an electron (either into the vacuum state or a neighbouring lamella, electrons) or free a hole able to move along a regularly arranged chain and to return the polymer chains around the site from which the carrier moves back to their original state.

However, when the charge carriers form a plane of charge, such as is found for the fast pulses after allowance for the spatial resolution of the detection system, their combined electric field will produce a mechanical compression in the polymer in front of the plane composed of mechanical relaxations of the  $\gamma$  and  $\beta$  types.

The compressive displacement  $\Delta R$  produced by an incremental field  $\Delta E$  additional to the applied field  $E$  has been found to be given by, [5]:

$$\Delta R = KE\Delta E \quad (2)$$

for polyethylene  $K = 1.56 \times 10^{-23}$  V<sup>-2</sup> m<sup>3</sup> [20].

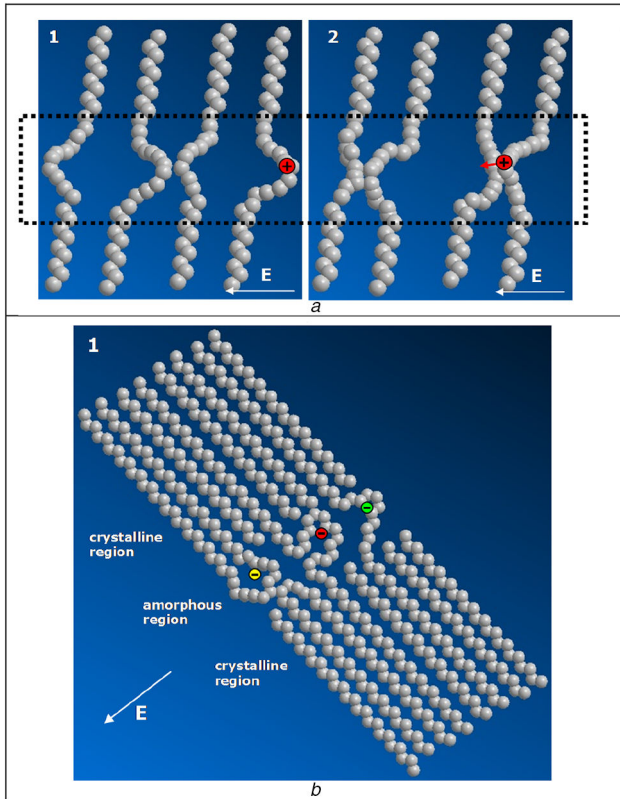
Under the assumption that the fast pulses are a plane of charge  $\Delta Q$  with area  $A$ , the incremental field is given by

$$\Delta E = \frac{(\Delta Q/A)}{2\epsilon_0\epsilon_r} \quad (3)$$

Positive pulses in the polyethylene at  $E = 40$  MV/m have  $\Delta Q/A \approx 2 \times 10^{-5}$  C/m<sup>2</sup>, which gives  $\Delta E = 0.49$  MV/m and a compression  $\Delta R \sim 0.3$  nm. This value of  $\Delta R$  corresponds to the 180° molecular rotations of a chain kink that occur in the  $\gamma$  relaxations of XLPE (see [7, 10] and references therein). Such molecular displacement can be envisaged as bringing the neighbouring chains close enough together (i.e. separation of  $\sim 0.05$  nm) to enable an effective tunnelling transfer of a hole between the chains, Fig. 6a, all across the planar front of the charge pulse. Relaxation of the chains carrying the positive charge as the compression boundary advances carries the charged plane a distance of  $\sim 0.3$  nm and subsequent repetition of the process allows the positive pulse to move through the material in steps of  $\sim 0.3$  nm as long as the planar nature was retained such that the compression boundary could be retained, i.e. the charge pulse can only move this way if it moves coherently. The value of  $\Delta Q/A$  in the positive pulse can, therefore, be seen to be the minimum quantity that is required to generate a compression boundary able to allow fast transport for positive hole carriers. The sequence of activated  $\gamma$ -displacement enabling tunnelling transfer and subsequent molecular relaxation can be combined into expression (4) for the positive pulse mobility, see [10] and references therein:

$$\mu = \frac{eR_s^2}{h} \exp\left(-\frac{\Delta\gamma}{kT}\right) \exp(-2\alpha R_t) \quad (4)$$

Here  $h$  is Planck's constant,  $\Delta\gamma$  = activation energy of the  $\gamma$ -relaxation,  $R_s$  = compression displacement (transport distance; 0.3 nm for  $E = 40$  MV/m),  $\alpha$  = tunnelling coefficient,  $R_t$  = tunnelling distance ( $\sim 0.05$  nm) between chains. A good fit, [10], to the data of Fig. 3a was found using a tunnelling barrier appropriate to polyethylene chains, with the difference between the data of 50 MV/m and that of 40 MV/m arising from the increase in compression, ( $R_s$ ), (2).



**Fig. 6** Schematic description of positive (a) and negative (b) ultra-fast pulse motion in polyethylene

(a) 1, 2: holes in positive pulse tunnel from one chain segment to another due to  $\gamma$  relaxation which causes  $180^\circ$  kink rotation, (b) Electrons in negative pulse move through free volume opened by  $90^\circ$   $\beta$  chain relaxation

The negative pulses have a value of  $\Delta Q$  that is a half of that of the positive pulses and according to (2) will only generate a compression of  $\sim 0.15$  nm at 40 MV/m. This amount of displacement is consistent with a  $90^\circ$  rotation of chain segments in the amorphous regions that can be associated with the  $\beta$  relaxation of XLPE. This relaxation is active when the material is in its rubbery state and so it can take place at temperatures above its glass transition, which is then case of the experiments reported here. Such displacement has the effect of opening up access to neighbouring free volume for electrons trapped on one side of it interface, [16], by removing barriers imposed by steric hindrance, Fig. 6b. The electron can then move freely into the neighbouring free volume region where it is again trapped [16, 20]. In this case, electron tunnelling is not involved and the corresponding mobility becomes, see [10] and references therein:

$$\mu = \frac{2kTR_s}{hE} \exp\left(-\frac{\Delta\beta}{kT}\right) \sin h\left(\frac{eER_s}{2kT}\right) \quad (5)$$

Here the transport distance of the electron is the distance from a free volume region to its neighbour, so  $R_s \sim 5$  nm and the energy gain of the electron in the applied field ( $eER_s$ ) is not negligible, unlike the corresponding value for the positive carrier. In this situation  $\sinh(eER_s/kT) \approx \exp(eER_s/kT)/2$  and (5) fits well with the experimental data of Fig. 3b, including the slight reduction of the activation energy with applied field. Again the amount of charge in the negative pulse produces a field that is just enough to force sufficient compression from the  $\beta$  relaxation to enable the electrons in the plane of charge to move coherently into the neighbouring free volume on the compression boundary. This transport process utilises a different mode of polymer relaxation to that of the positive carriers and places the electrons in different locations to those of the positive holes i.e. bound near to polymer chains in free volume regions, [16], as opposed to located within chain kinks in more dense parts of the amorphous region where chain to chain transfer can take place [14, 18, 19]. Consequently, negative and

positive pulses can be expected to coexist and to pass through one another without recombination.

Charge pulses of this type have their carriers in trap sites located in the lamella amorphous interface in the form of a plane of charge. Their fast speed of movement arises from the electro-mechanical deformation produced by the electrical field of the charged plane that allows the carriers to transfer through the amorphous region and around the lamella-amorphous interfaces at rates that are orders of magnitude faster than those applying to promotion of the carrier to a free (vacuum or lamella) state, in which it can transfer independently to a neighbouring interface trap (conventional conduction mechanism). The pulses retain their coherence as a plane in two ways. First, the fast transport inhibits the much slower individual movement and second the long range polarisation of the polymer by the plane of charge generates a potential surface that holds the carriers together in the form of a soliton [15]. The formation of the electro-mechanical deformation is crucial to the ability of the pulse to move rapidly. The extent of the deformation is determined by the sharp front of the plane of charge and the speed with which it is formed depends on the activation energies for each contributing relaxation mode. Thus as the temperature increases, the deformation generation rate and thus, the speed of the pulse increases as shown in Fig. 3.

The pulses are formed by charge injection from the electrodes in a very similar way to that in which they move. At the electric fields for which they have been observed injection is by tunnelling from the electrodes, [10], rather than the field-assisted Schottky injection process, [2], that dominates at fields of  $\sim 100$  MV/m and above. During injection, the amount of charge builds up to that required for fast coherent transport and the charged plane moves forward faster than the charges can spread out by incoherent movement. As the pulse moves forward the tunnelling distance between it and the electrode increases and reduces further injection to the pulse plane to a negligible amount [10] leaving the quantity of pulse charge unchanged. At the same time, the electric field behind the pulse is reduced and the polymer is expanded thereby increasing the tunnelling distance so that further injection cannot produce another pulse until the first one has moved much further into the polymer, and the polymer morphology at the electrode has recovered its original state.

#### 4 Conclusions

The theory of carrier transport in insulating polymers has hitherto relied on concepts transferred from semiconductor crystalline materials, albeit with a large band gap. Here we have shown that their flexible nature can introduce new behaviour. It can change the incoherent trap-to-trap transport of charge carriers in semiconductors to a coherent form of transport, in the form of a plane of charge of either polarity. This happens in electric fields for which charge injection from the electrode occurs but is relatively small. The pulse is both formed and moves coherently as a result of the electro-mechanical compression at its boundary, i.e. as a result of the polymer flexibility. This results in mobility enhanced by a factor of about  $10^5$  above that of the incoherent trap-to-trap transfer. Although this mobility is of the order of  $10^{-6}$ – $10^{-9}$  of that of carriers in semiconductors it allows the pulses to transit a typical insulation thickness within a few seconds, where, because of the non-ohmic nature of the electrode–polymer interface, it builds up a heterocharge field that could pose a risk to the integrity of the insulation in DC fields. In contrast to this deleterious feature the phenomenon, however, opens up the exciting possibility of the construction of a flexible biomimetic system. The speed of the pulses is very similar to that of the action potential in nerve axons, [20], and so each pulse could be regarded as carrying a unit of information. On reaching an intermediate electrode the step-wise build-up of heterocharge, and hence of electrode field, could be used to trigger new pulses in a different section of polymer depending upon the amount of charge that has arrived, rather like synapses in a nerve system.

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