CHARGE INJECTION, ELECTROLUMINESCENCE, AND AGEING OF AN EPOXY RESIN IN HIGH DIVERGENT FIELDS

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INTRODUCTION

Most experimental studies of electrical ageing have concentrated on semi-crystalline polymers such as those used in cable insulation and capacitors (see for example [1]). Theoretical models [2-4] for electrical ageing have been developed on the basis of these studies. The consensus is that ageing involves the formation of low-density regions, though the mechanisms responsible are disputed. For example, bond scission by high-energy electrons [2,5], and mechanical deformation have both been suggested. Both of these mechanisms are related to charge injection and the subsequent formation of high local fields. The semi-crystalline polymers studied so far have similar chemistries and almost identical morphologies. They tend, therefore, to show many similarities in, for example, the size of the energy barriers for the ageing reaction, critical ageing levels, and field dependence of ageing [4]. These similarities make it difficult to discriminate between mechanisms. Epoxy resins, however, are network polymers with a different molecular chemistry to that of the semi-crystalline polymers and are thus ideal to evaluate the proposed ageing mechanisms. We have therefore studied an epoxy resin (CY1301) under both uniform field and high divergent field conditions. Uniform field conditions were used to gain baseline characteristics for the properties of the unaged epoxy resin, and also for the effects of electrical ageing in low fields. Studies in high divergent fields were made using an electrode arrangement adapted from that of [6]. A number of wires set approximately *0.5mm* apart were embedded, parallel to the flat faces, in thin (~290 μm) flat samples. The radius of the wires ranged from 5 μm (gold plated tungsten) to 25 μm (tungsten). Relatively small voltages applied to the wires (≤5 kV DC) therefore produced local fields up to 170 kV/mm depending upon the wire radius chosen. These field levels are high enough to inject space-charge [6] without leading to instantaneous failure. This geometry, therefore, may both inject charge and simulate local stress enhancements arising from charge accumulation. The number of wires is large (~30) so that the volume affected is big enough to allow changes on ageing to be detectable.

EXPERIMENTAL INVESTIGATIONS

Dielectric Response

The dielectric response of the epoxy exhibited a glass transition just below 40˚C [7]. At this temperature and above a loss peak was observed at low frequencies that merged into a power law response at higher frequencies and eventually into a high frequency loss peak at ~3 10^5Hz. A dc conductivity masking the low frequency side of the alpha peak was observed at T≥70 ˚C, figure 1. An Arrhenius plot of the low frequency peak show the approach to zero frequency typical of the alpha response of a glass transition, figure 2. The power law response is less clear-cut as it is partially obscured by the two peaks surrounding it. Ageing in uniform field progressively reduced the power law component, figure 3a. A similar reduction of the loss component C" in this frequency region was found when the ageing was carried out in divergent fields (7 days with –2 kV applied to 50 μm diameter tungsten wires), figure 3b. Here the dielectric measurement was carried out both between the two plane electrodes and between the wires and a plane electrode. The results differed only by a multiplicative factor arising from the different geometries.

Current-Voltage Measurements

Uniform Applied Fields. These measurements were performed on samples 55 μm thick using a step ramp technique. The dwell time was *300s* on the ascending ramp and *150s* on the descending ramp. The current was averaged after the first *50s* of the dwell time and was measured simultaneously with the electroluminescence (EL). The ascending ramp shows a linear I-E dependence up to 140 kV/mm, and thereafter a strongly field dependent current up to 300 kV/mm. In the experiment the sample was cycled to progressively higher applied fields. It was noted that the current in the ohmic region varied from cycle to cycle whereas that in the high field region was effectively unchanged. Figure 4 shows the current obtained on the final cycle. The high field current could be described empirically by an E^4 law, but it also fits an exponential dependence appropriate to charge hopping between neutral traps, i.e. $I \propto \left[\exp(aeE/kT) - \exp(-aeE/kT)\right]$, see figure 4. The estimated value of *a* is 0.52 nm, which is acceptable for this kind of mechanism. The descending ramp shows a reverse current that changed sign below 220 kV/mm, indicating the presence of a zero-field plane in the dielectric at and below these applied fields as a consequence of the strong charging occurring on the ramp-up.

Space Charge Measurements

In Uniform Applied Fields. The pulsed electro-acoustic (PEA) technique was used to measure the space charge generated in the epoxy under uniform fields applied by brass electrodes. The form of the space charge distribution observed depended upon the duration of the period of electric stress and the temperature. Under short term stressing (1-6h) at room temperature (~25˚C) a field of ≥18 kV/mm was required before charge injection could be identified via the formation of homocharges near the electrodes, figure 5. Homo space-charge was also, however, produced by prolonged stressing (1day to 2 weeks) at lower fields, e.g. 7kV/mm. A similar behaviour was obtained at 35˚C, figure 6. At temperatures of 40˚C and above any space charge produced by prolonged stressing at low fields was obscured by the polarisation charges on the electrodes.

In Divergent Applied Fields. These samples were first measured at room temperature with 0.67 kV applied between the plane electrodes with the wires floating, figure 7a. No signal was observed from parts of the samples that contained no wires but a weak peak (approx. -0.5 C/m^3) was obtained around the region of the wires. A sample was then stressed by applying 1.5 kV to the wires for 1 week at 33˚C. The voltage was removed and the sample measured at 33˚C. A positive signal was observed across most of the sample rising to a peak of ~0.75 C/m^3 close to the wires, figure 7b. The signal persisted for at least 90 min at 33 ˚C. This result is consistent with the injection of positive charge from the wires that are retained in deep traps [8]. The contribution of a polarisation gradient [9] to the effective charge would be expected to give a similar signal but it should decay rapidly as the polarisation relaxed.

Electroluminescence Measurements

In Uniform Applied Fields. These were measured simultaneously with the charging and discharging currents. Continuous EL was observed to occur above –150 kV/mm dc when ramping up. When the voltage was ramped down EL ceased at –250 kV/mm dc, figure 8.

In Divergent Applied Fields. In the first instance a square voltage pulse of duration of 100 m*s* to 60 s was applied to the sample. Electroluminescence was observed at the beginning and end of the pulse if an onset voltage is exceeded, figure 9. The onset voltage ~400-500V corresponds to a field of 22-27 kV/mm if the wires are assumed to lie exactly in a plane midway through the sample. Continuous electroluminescence was not observed in these experiments even at the highest fields reached of 160 kV/mm. No appreciable polarity effect was found. A second set of experiments was carried out in which a train of positive probe pulses was applied following a negative polarisation pulse. The probe voltage level was chosen so that it did not excite any luminescence by itself. The delay time between the polarisation pulse and the 1st probe was varied with a minimum of 1 s. The repetition frequency of the probe pulses was also varied, but this parameter was not influential and most of the results were obtained by using a frequency of 1Hz. The luminescence intensity detected decreased throughout the sequence of probe pulses following on from the initial polarisation pulse. In these experiments the probe pulses detected luminescence up to several seconds after polarisation. A large scatter about a typical mean value of 60 s was observed with extremes of 35 s and 80 s. The period over which luminescence is detected ('decay' time) can be taken to be the time required for the space charge to reduce to a level below which it is incapable of exciting luminescence centres to a detectable extent. This interpretation is valid as long as the probe pulses themselves do not affect the amount of space charge existing at the time of their application. In order to check that this is indeed the case the delay time between the polarisation pulse and the 1st probe pulse was varied over the range 1 s to 16 s. The EL measured by the 1st probe pulse decreased (approximately exponentially with time) but the time for the EL to decay (i.e. decay time) was not altered appreciably. This indicates that the probe pulses did indeed act as true probes for the space charge field. No appreciable effect on the 'decay' time was observed when the polarisation pulse was varied in magnitude (from 2 to 2.8 kV) and duration (from 100ms to 60 s). This indicates that the process of charge injection and accumulation in the vicinity of the wires is saturated in a time less than 100 ms, and that the field dependence of charge injection is not very strong at these levels (108 to 150 kV/mm). This is in agreement with other workers [8]. It was also noted that EL was observed on the first two probe pulses even when the voltage of the polarisation pulse was set below the EL threshold of 500 V. This observation demonstrates that charge injection can occur without detectable EL, but its presence can be revealed when the probe pulse increases the local field. The need to increase the local field through the opposite polarity pulse implies that a true threshold field is required in order to generate EL in this case.

DISCUSSION

The PEA technique has shown that short-time space charge injection occurs in uniform applied fields above

18 kV/mm and in divergent fields of at least 52 kV/mm (at the wire) over a period of time. This latter measurement could be attributed to a positive polarisation gradient around the wires, however, the dielectric response shows that any polarisation should have relaxed within a few seconds, whereas the positive PEA signal has not decayed even 90 minutes after voltage removal. The signal therefore appears to be due to injected positive charge. This is confirmed by the transient EL data in divergent fields, for which the onset threshold field of 22-27 kV/mm correlates well with that found for injection in the PEA experiments.

These experiments also show that the common assumption that uniform field injection occurs at low fields because of local stress enhancing features on the electrode surfaces is not applicable in this case unless the injecting features are smaller in size than the 5 μm wire radius, e.g. crystalline boundary edges. Because of the presence of space charge at low fields we would expect to find a non-ohmic I-E dependence above 18 kV/mm in uniform fields. This is not the case. When the high-temperature low-field (3.5 V/mm) conductivity determined from the dielectric response is extrapolated to T=24 ˚C (activation energy = 1.6 eV) it yields a value (2.2 10^{-16} S/m) close to that found for fields up to 140kV/mm (i.e. ~ 5.2 10^{-17} S/m). This implies that space charge injection does not modify the conductivity very much in the experiments performed at uniform fields up to ~140 kV/mm. The high activation energy for the linear conductivity indicates that charge transport is dominated by hopping between neutral deep traps. Hence, in the thin samples, injected charge may be trapped close to the electrodes to form a virtual electrode during the dwell time at a given voltage. The dielectric thickness would then be reduced slightly giving an actual electric field that would be slightly higher than the applied field but still uniform.

A possible explanation of the transient EL observed in divergent fields lies with the excitation of luminescence centres by inelastic scattering of the injected carriers up to the point where a sufficient amount of charges have been trapped in the vicinity of the wire to counterbalance the injecting field. On depolarisation the field at wires has the same magnitude as the applied injecting field but in the opposite direction. Consequently the same EL excitation occurs on extraction and with essentially the same magnitude. The absence of continuous dc EL is in accordance with a transient injection process limited by the space charge field. An alternative mechanism based on discharges in sub-micro sized mesovoids cannot be ruled out, however, without a spectral analysis of the EL emission. Conversely, a continuous EL emission is found for uniform applied fields above 160 kV/mm. At these fields, different continuously operating excitation mechanisms can be invoked e.g. charge packet generation leading to a recombination front between positive and negative charge carriers [10]. It is noteworthy that the EL onset-corresponds to the change from the ohmic to the non-linear regimes in the current measurements. This correlation has previously been reported for different polymeric materials submitted to a dc field [5]. It indicates that the high-field conduction process drives the excitation of EL. Our observation of an exponential field-dependence of the conductivity indicates a trap-to trap hopping mechanism for the mobile carriers that enables the charge packet to advance in the form of an ionisation front [11]. Further work is, however, needed to determine the details of the relationship between current and EL in epoxy resins.

The maximum applied field achieved so far in the divergent field geometry only just reaches the onset value for continuous EL in uniform applied fields and does not generate continuous EL. Transient electroluminescence is, however, observed on polarisation and depolarisation at fields above an onset value. The results of the probe-pulse experiments indicate that even below the onset field for transient luminescence, the applied voltage generates space charge. At these fields the PEA experiments show that some space charge can be generated given sufficient time. These charges can produce luminescence when a sufficiently large pulse of opposite polarity is applied. It is noticeable that luminescence occurs when the sum of the polarisation voltage and the probe voltage is sufficient to exceed the EL onset field found in the single pulse experiments. The quantity of charges available to produce luminescence decays rapidly with time (time constant ~ 10.5 s). It therefore appears that the charges have a non-radiative form of neutralisation, with luminescence only occurring when the local field exceeds a level sufficient for rapid charge injection or extraction. These results associate the luminescence with charges possessing a high kinetic energy, i.e. those charges that initiate EL via inelastic scattering. In lower fields extraction or non-radiative recombination can proceed without luminescence. This would be consistent with the observation that the onset fields and field dependence of electroluminescence are the same for the polarisation and depolarisation transients in both positive and negative polarity.

The evidence for ageing under the influence of electric fields high enough to inject space charge comes from two directions. In the first instance there is reduction of the intermediate power law response in the dielectric response. The epoxy used was cured at room temperature and thus had a T_g about 10 °C lower than if it had been post-cured at high temperature. However, the change cannot be assigned to a global increase of T_g by additional cross-linking, as the alpha-response is not affected. Power law dielectric responses have been associated with a hierarchy of relaxing dipoles embedded within one another in a self-similar form (e.g. see [12]). Fragmentation of such a hierarchy such as to reduce the number of embeddings, will reduce the frequency range of the power law dependence. The removal of this response on ageing would thus be attributable to a fragmentation of the self-similar system; probably by additional cross-linking which would break connections in the hierarchy of relaxations. The second instance of ageing relates to charge injection on long time exposure to fields below the short-time onset threshold. It is not clear what is happening here, except that the factors influencing charge injection are being altered over a period of time. Possibly ionically dissociated species migrate slowly to the electrode in the electric field and produce heterocharge that eventually builds up sufficiently to induce homocharge injection. A process like this can also be expected to cause material changes over a long period of stressing in consequence of injection currents and local field modification. The changes in the ohmic current that are observed during voltage cycling may provide further evidence that changes are introduced by exposure to high fields. A systematic investigation is, however, required in order to verify this effect.

CONCLUSIONS

- Charge injection in both uniform and divergent fields has been observed. The onset field for injection in both cases is essentially the same and equal to the onset field for transient electroluminescence.
- Charge injection at these fields has been shown to reduce the response of certain set of re-orientable dipoles in the epoxy resin.
- Long term stressing at lower fields can lead to charge injection even at fields below the onset threshold for short-term injection and electroluminescence.
- A high field conduction process involving trap-to trap hopping is associated with continuous EL.

ACKNOWLEDGMENTS

The authors would like to thank Dr. J. Alison (King's College London), Prof. J. Champion and Dr. S. Dodd (London Guildhall University) for their useful discussions and practical assistance.

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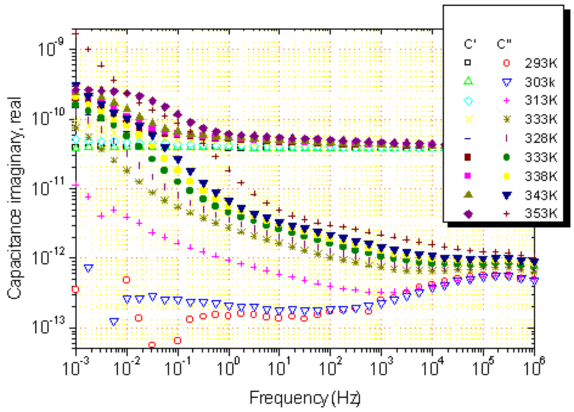

Figure 1. Dielectric response measured for a range of temperatures.

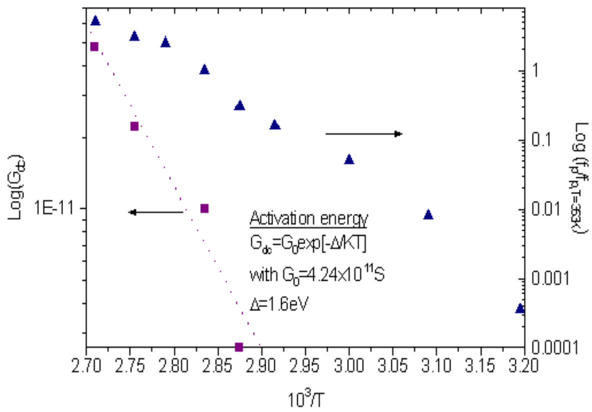

Figure 2. Arrhenius plots of the relative position of the alpha dielectric response ▲ (Right Hand Scale) and the conductance ■ (Left Hand Scale)

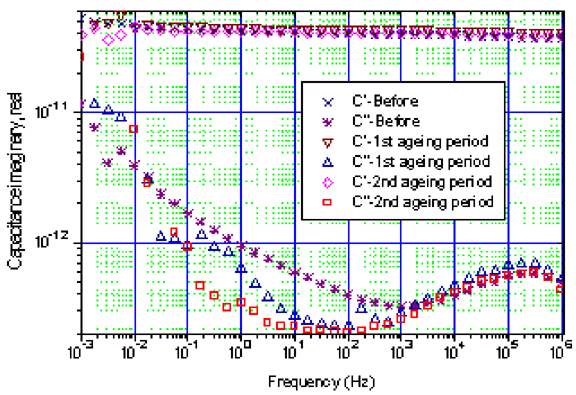

Figure 3(a) Dielectric response of epoxy resin at 40 °C before and after ageing in a uniform field (72h/34.5kV/mm at 35 °C + 47h/51.7kV/mm at 40°C; second curve for additional 47h/51.7kV/mm at 40°C)

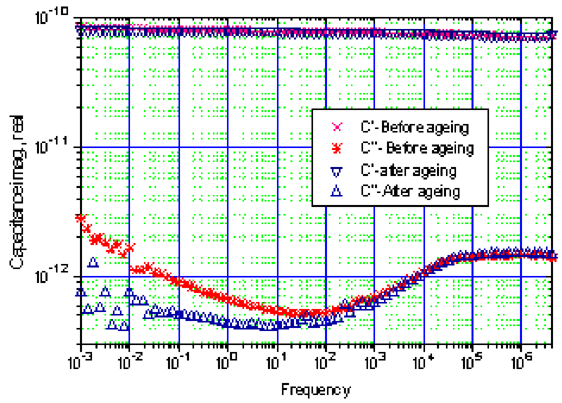

Figure 3(b) As Fig. 3(a) but in a divergent field at 20°C.

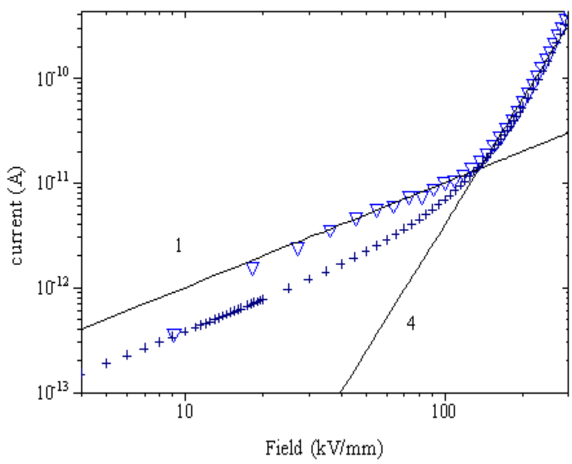

Figure 4. I-E plot for the ascending ramp ▽. Continuous line, power law fit, crosses (+) exponential fit

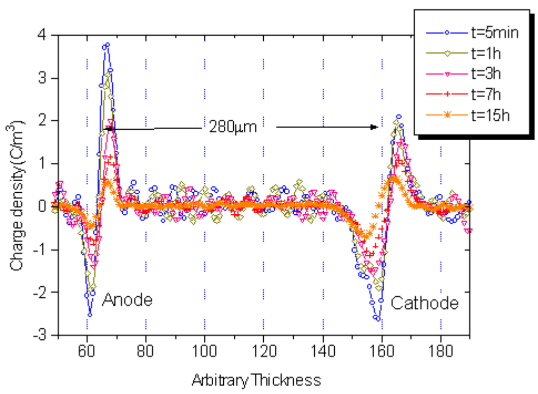

Figure 5. Space charge distribution measured following voltage removal after 1h under a uniform applied field of 18kV/mm at room temperature. Horizontal scale is time in ns and converts to distance on multiplying by acoustic velocity. The times at which measurements are made after voltage-removal are shown inset.

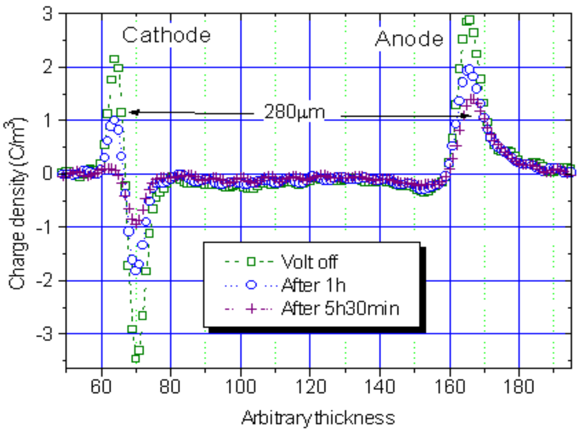

Figure 6. Space charge distribution observed on voltage removal after a polarisation time of 42h under a uniform applied field of 7kV/mm at 35°C. Horizontal scale is time in ns and converts to distance by multiplying by the acoustic velocity.

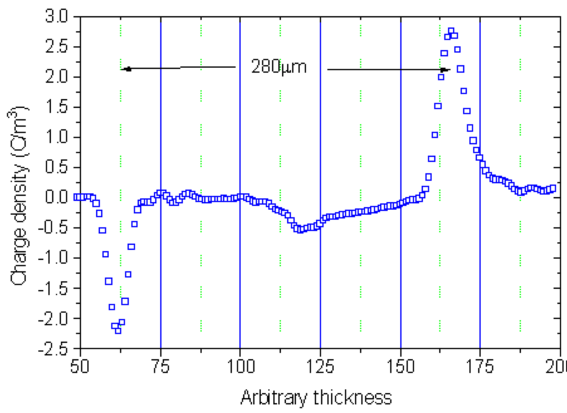

Figure 7(a) Space charge distribution obtained by applying 0.67kV between the plane electrodes with the wires floating.

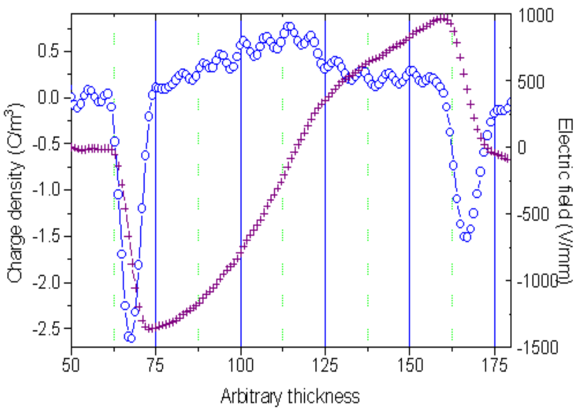

Figure 7(b).Space charge distribution measured at 33°C following 2 weeks with 1.5kV applied to the 25µm diameter gold plated tungsten wires at 33 °C. Left hand scale gives the charge density and the right hand scale the derived field.

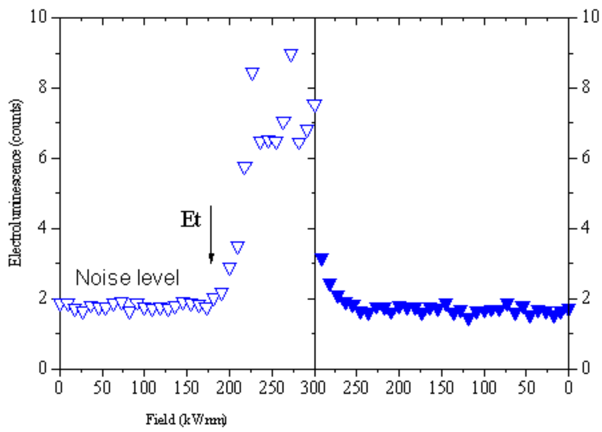

Figure 8. Electroluminescence counts as a function of field during ramp-up ▽ and ramp-down ▼. Noise level = 2 counts.

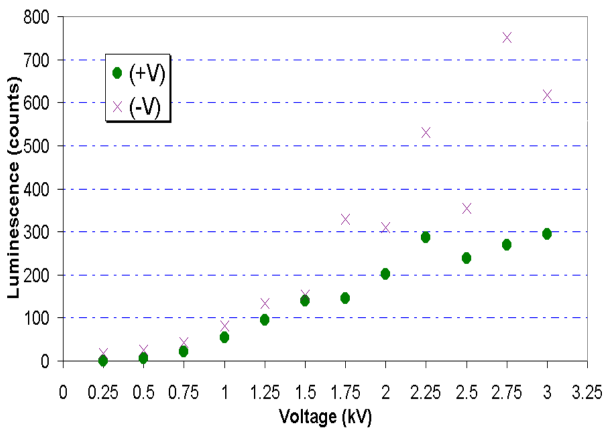

Figure 9. Electroluminescence counts. Positive pulses (•), and negative pulses (6).