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Charge transport and accumulation in clay-containing LDPE nanocomposites

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Charge Transport and Accumulation in Clay-containing LDPE Nanocomposites

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ABSTRACT

This paper discusses the charge transport and accumulation in clay-containing LDPE (Low Density Poly-Ethylene) nanocomposites. LDPE is shown to host charges of both polarities in the form of homo and heterocharge when subjected to high electric fields. Addition of nanoclays has been shown to always increase the high field DC conductivity of the nanocomposites. This is shown to actually work in favor of the ability of the material to prevent the accumulation of space charge by slowly, but persistently, allowing space charges to flow across the insulation wall. However, in severe conditions of a combined high electric field and high temperature, the current flow exceeds a threshold where massive injected charges negatively impact the charge profile and the electric field distribution is heavily distorted.

Index Terms — conductivity measurement, space charge, PEA, electric field distortion

1 INTRODUCTION

UNDERGROUND and submarine cables are important components in the power grid for the transmission and distribution of electricity and it is of vital importance that they should function reliably for many years. To reach this goal and further improvements in transmission capacity, efforts must take place to improve the insulation layer as the heart of the HV cable. In recent decades polymeric extruded insulation cables have been gained attentions in this regard. In particular, the cross-linked polyethylene insulation cables or XLPE has become the primary cable insulation material for both high voltage AC and DC applications because of its mechanical flexibility, thermal endurance and excellent dielectric properties [1]. Despite all the advantages, XLPE cables can suffer from several problems such as thermal degradation and the lack of recyclability [2]. Those employed for high voltage direct-current (HVDC) applications have also been shown to have the tendency to accumulate space charge, which can lead to failure, especially when encountering polarity reversal operations [3]. Interests have been expressed as to improve the performance of HV cables as the use of XLPE cables grew. Nanometric dielectrics, or nanodielectrics, consisting mainly

23 of a polymeric matrix and a nanometric reinforcement have
24 been the subject of many researches in recent decades. A great
25 choice of nanoreinforcement is layered silicate fillers, for
26 which many nanocomposites have been produced and
27 analyzed. The incorporation of small percentage of nanoclay
28 has shown to improve the thermal and mechanical properties
29 of polymers [4]. They are also reported to have superior
30 electrical breakdown strength [5], improved partial discharge
31 and volume resistivity to erosion [6, 7] but always higher
32 dielectric losses at power frequency [8] comparing to unfilled
33 polymer.

34 In addition, mitigation of space charge accumulation can
35 potentially be reached with such nanocomposites which is of
36 vital importance since less accumulated space charge in the
37 insulation material allows for higher applied electric field at
38 the same cable geometry and as a result the weight and cost of
39 power equipment will be decreased. This can be possible due
40 the barrier effect of the clay platelets, ioning trapping of the
41 inorganic filler and also a slight increase of the DC
42 conductivity allowing space charges to slowly flow across the
43 insulation wall instead of accumulating inside the insulation
44 bulk. Thus, understanding the space charge behavior of clay-
45 containing polymers is of necessary for designing new
46 materials for HV applications.

47 This manuscript is a continuation to the authors' previous
48 work where it was shown that the addition of clay nanofiller

1 significantly improves the AC electrical breakdown strength
2 of LDPE, while always results in inferior, but comparable, DC
3 electrical breakdown properties [5]. This investigation
4 resumes in this report by evaluating the charge transport and
5 accumulation within the same materials to have a general view
6 of their potential for applications as insulating walls in HV
7 cables or for other applications for which surface or internal
8 charging is an issue such as spacecraft dielectrics [9].

2 EXPERIMENTAL

2.1 MATERIAL AND PROCESSING

11 A premixed LDPE/Clay commercially available masterbatch
12 was diluted with pure LDPE in powder form to achieve clay-
13 containing LDPE nanocomposites with desired concentrations
14 of nanofiller (1%, 2.5%, 5%, 10% and 15%) in a co-rotating
15 twin screw extruder. The masterbatch contains nominal 50 wt
16 % of montmorillonite clay which has been treated with
17 compatibilizing agents to enhance their dispersion within the
18 polymers. The obtained pellets were then press-molded into
19 thin plates with thickness around 280 μm . Morphology of the
20 as-obtained nanocomposites were investigated in the authors'
21 previous work where it was shown in SEM images that stacks
22 of nanoclay are uniformly distributed throughout the
23 polyethylene matrix. Further observation through TEM images
24 revealed clear signs of polymer intercalation where numerous

individual high aspect ratio clay platelets were spotted
separated from each other and partial exfoliation is achieved
(Figure 1). The apparent orientation of the nanoparticle was
related to the high pressure and high temperature condition of
the molding process of pellets into thin plates. The readers are
referred to the authors' previous work for detailed information
about the materials, nomenclature and experimental procedure
[5].

2.2 CHARACTERIZATION

34 Conduction current measurements were conducted using a
35 three electrodes system under a field of 50 kV/mm at 30 $^{\circ}\text{C}$.
36 Supplementary measurements have been conducted on neat
37 LDPE and LDPE/2.5C nanocomposite (containing 2.5%
38 nanoclay) under different fields (30, 40 & 50 kV/mm) and
39 different temperatures (30, 50, 70 & 90 $^{\circ}\text{C}$) to evaluate the
40 effect of temperature and field variations. Samples were
41 sputtered by gold prior to testing. The system is consisted of
42 main and guard electrodes on one side, and a counter electrode
43 on the other side. The whole system was placed in an oven,
44 where the temperature was stabilized before starting the test.
45 The measurement lasted until the steady state conduction was
46 achieved which took an average time of 24 hours for each
47 sample. An average of the last 100 points after stabilization
48 was considered as the conduction current. Charging and
49 discharging current was continuously monitored using a
50 digital electrometer (Keithley 6514) and the system was
51 computerized using a Labview application.

52 Pulsed Electroacoustic technique (PEA) has been used to
53 measure the space charge profile under the application of DC
54 electric fields. In this method the interaction of a pulsed
55 electric field and space charges inside the sample creates
56 acoustic waves that propagate through the sample to be
57 detected by the transducer. In order to attenuate sonic
58 impedance mismatch, a semiconductive layer was placed
59 between the specimen and HV electrode. While samples were
60 experiencing the DC field for a duration of 10000 s in the
61 polarization stage, a HV pulse with an amplitude of 500 V and
62 duration of 10 ns was applied to collect the charge profile
63 information within the specimen. At the end of the
64 polarization phase, the HV source was short-circuited to
65 record the depolarization profile for a duration of 3000 s. The
66 space charge measurements have been conducted on different
67 samples at ambient (25 $^{\circ}\text{C}$) and higher (60 $^{\circ}\text{C}$) temperature
68 under different electric fields.

3 RESULTS AND DISCUSSION

3.1 ELECTRICAL DC CONDUCTIVITY

71 High-field DC conductivity measurements are important to
72 gain understanding of conduction mechanisms of insulating
73 materials especially for their usage in HVDC extruded cable
74 systems. Polarization (charging) currents of neat LDPE and its
75 clay-containing nanocomposites over time at 30 $^{\circ}\text{C}$ and under
76 50 kV/mm electric field are depicted in Figure 2a. The
77 calculated corresponding DC conductivities from the
78 measured conductive current after achieving the steady state
79 are shown in Figure 2b. For neat LDPE, the polarization
80 current immediately decreases by three decades which

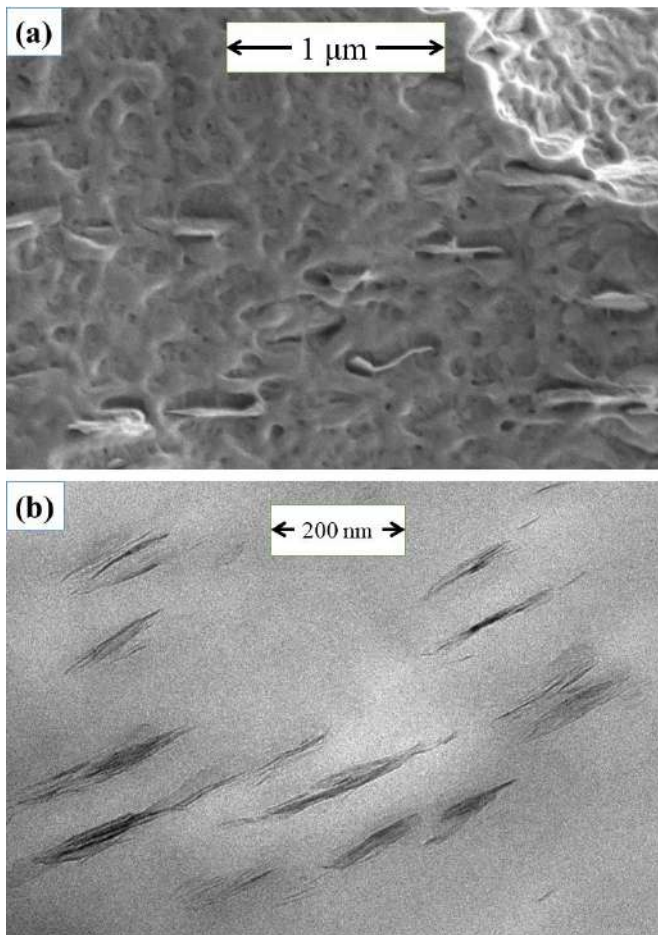


Figure 1. Micrographs of LDPE/5C: a) SEM and b) TEM. (Images are taken from authors' previous work [5])

1 corresponds to the fast polarization. It then gradually 26
 2 decreases over time, corresponding to slow polarization, and 27
 3 after around 24 h the steady state is achieved and the current is 28
 4 believed to be fully conductive. The calculated conductivity 29
 5 for LDPE at 50 kV/mm is around 1×10^{-15} S/m which is close 30
 6 to the values reported in the literature [10]. Upon addition of 31
 7 clay, there is a significant increase in the level of high-field 32
 8 conductive current and hence the high-field DC conductivity. 33
 9 There is more than 2 decades increase in conductive current 34
 10 when only 1% of clay is incorporated, and it continues to 35
 11 increase towards higher percentages of clay. From 5 to 10% of 36
 12 clay loading, there is an increase of almost three decades of 37
 13 current and the DC conductivity reaches to 1.9×10^{-12} S/m 38
 14 when 15% of clay is incorporated. The presence of a 39
 15 maximum value in the time dependence of the current for the 40
 16 LDPE/1C nanocomposite is in good agreement with the space- 41
 17 charge limited current theory and also in agreement with the 42
 18 numerical solution of the transport equations when trapping 43
 19 and detrapping of charge carriers are taken into account and 44
 20 when Schottky conditions are used at the electrodes [11]. It 45
 21 also appears that under high electrical field, a sharp increase of 46
 22 the conductivity, similar to a percolation threshold, is already 47
 23 achieved at a concentration of 1 wt% (which wasn't observed 48
 24 at lower field). Very low percolation thresholds are typical of 49
 25 high aspect ratio inclusions. They are indeed commonly 50

observed in the case of CNT-based composites [12] and can
 also be predicted by Monte Carlo simulation of composites
 filled with circular nano-disks [13].

On the other hand, reductions in electrical conductivity of
 nanocomposites have been reported several times for
 nanocomposites containing metal-oxide nanoparticles [14-16].
 The main explanation given is that during the cooling stage,
 the polymer molecules are encouraged to regain the natural
 polycrystalline morphology where hydrocarbon chains form
 planar crystalline lamellae 10-20 nm thick and ~100 nm wide
 growing out from nucleation points to form spherulites.
 Growing crystalline lamella will reject the particles, impurities
 and entangled polymer chain structures to form inter-lamella
 amorphous phase. In case of nanometric particles, such as
 metal-oxide, some particles might be left in the inter-
 crystalline amorphous phase as crystallization proceeds that
 will strongly influence the hole/electron tunneling between
 lamella across the amorphous phase. Due to the difference in
 the band gap of the most metal-oxide nanoparticles with
 polyethylene, additional potential barriers are involved which
 results in increased mean tunneling barrier and lowered local
 hole inter-lamella transition rate [17]. Consequently, the
 overall macroscopic mobility and conductivity is lowered. The
 number of affected transition depends on the average diameter
 and concentration of the nanoparticle.

In case of layered silicate, such as montmorillonite clay, and
 due to the high aspect ratio and the tendency to form stacks
 and agglomerates, they are not expected to be included in the
 inter-lamella regions. Instead, they are most likely
 accommodated in the inter-spherulite region and therefore,
 will not engage directly in a hole or electron tunneling process
 between crystallites at the nanometric level. The increase in
 the conductivity of nanocomposites can be more simply
 related to the formation of high field conductive paths and the
 increase of mobile charge carriers including free ions
 introduced by clay nanoparticles due to mobile ion scavenger
 capability of nesosilicates dispersed within the polymer
 matrix. It should be noted that the connectivity criterion
 changes from low field to high field since hopping between
 inclusions is strongly field-dependant.

Since the crystallites do not support ionic transport, the
 remaining ionic path is in the amorphous phase where the
 majority of clay nanoparticles are located. The structural
 symmetry due to the intercalated structure and the huge aspect
 ratio of clay nanoplatelets even more facilitate the conduction
 path and make it possible to obtain a massive increase in the
 conductivity even at low concentration of nanoclay. It should
 also be noted that even if ionic conductivity is involved in the
 early conduction process, the long term steady-state current is
 essentially due to electronic conductivity that takes over after
 the ionic species reach an equilibrium state resulting in
 electrode polarization.

DC conductivity in polymeric material is temperature and
 electric field dependent and one way to express this
 dependency is to use the empirical equation below [18]:

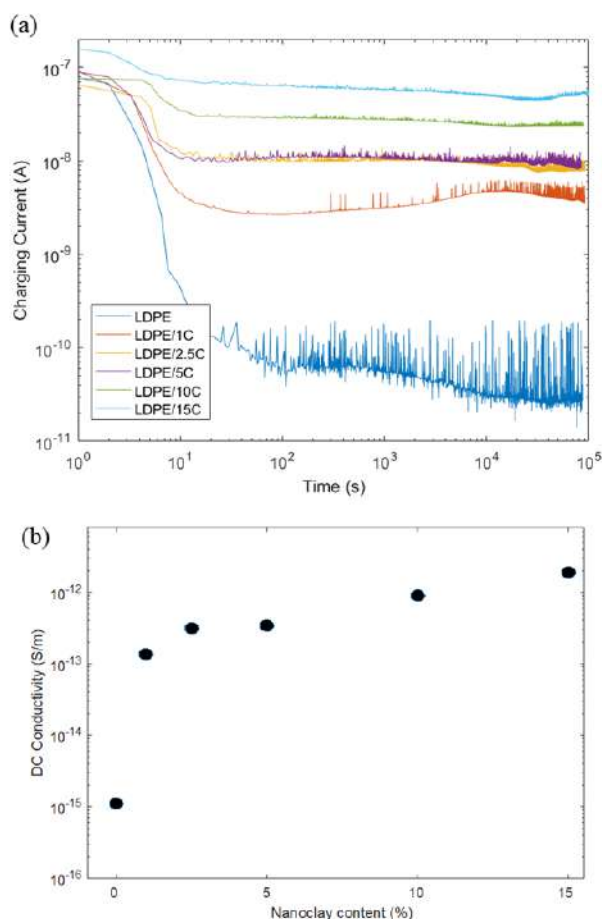


Figure 2. a) Charging currents of LDPE and its nanocomposites at 30 °C and under applied DC electric field of 50 kV/mm; b) calculated DC conductivities from steady state part of the charging currents.

$$\sigma = \sigma_0 \exp(\alpha T) \exp(\beta E) \quad (1)$$

Where α and β are the temperature and electric field coefficients respectively. The dependency to electric field is shown in Figure 3a where the DC conductivities for neat LDPE and LDPE/2.5C nanocomposite are illustrated at 30 °C and under different fields: 30, 40 and 50 kV/mm. The DC conductivity for LDPE remains almost the same while it monotonously increases for the nanocomposite. According to equation (1), the estimated electric field coefficients for LDPE/2.5C is almost ten times higher than that of neat LDPE ($\beta_{2.5C}=0.132$ mm/kV, $\beta_{LDPE}=0.014$ mm/kV). Another way to express the dependency of the DC conductivity towards electric field is the use a power law relationship [19]:

$$\sigma = \sigma_0 \exp(\alpha T) E^\beta \quad (2)$$

The experimental results fit as well equation (2) with the same field coefficient ratio ($\beta_{2.5C}=5.49$, $\beta_{LDPE}=0.55$). More complex equations expressing the direct conductivity as a function of both field and temperature can be found in the literature [20]. It

appears that electric field variation directly influences the conductivity of nanocomposite and a stronger applied field enhances the mobility of charge carriers to drift/migrate to the opposite electrode rather than accumulate at the interface region. The dependency to temperature is shown in Figure 3.b where the DC conductivities of neat LDPE and LDPE/2.5C nanocomposite are illustrated under 50 kV/mm of electric field at different temperatures: 30, 50, 70 and 90 °C. Applying equation (1) fits well to the experimental results if the low temperature DC conductivity of the nanocomposite is ignored. The temperature coefficients have almost similar values ($\alpha_{2.5C}=0.083$ K⁻¹, $\alpha_{LDPE}=0.074$ K⁻¹) indicating that temperature variation effect is mostly controlled by the matrix not by the nanofillers. Generally, it is believed that the conductivity of polymers is thermally activated and Arrhenius-type model can describe this physical phenomenon:

$$\sigma(T) = \sigma_0 \exp(-E_a / kT) \quad (3)$$

where σ_0 represents the pre-exponential factor, E_a represents the activation energy and k represents the Boltzmann constant. The estimated activation energy for LDPE/2.5C is slightly higher (0.84 eV) than that of neat LDPE (0.7 eV). However, four points of data are certainly not enough to accurately estimate the activation energy. It was reported in the literature that above 45 °C the activation energy of LDPE changes from 1 eV to 0.6 eV [21]. This may also explain the low temperature deviation noted for LDPE/2.5C.

The increased DC conductivity at higher temperatures following an exponential relation can readily be explained referring to bulk limited conduction mechanisms for which the material is represented by a series of potential wells with given depth and separation. The conduction process then relies on thermally assisted hopping between localized states, which leads, after some approximations, to the exponential expression given in equation (2). Much more detailed (and more sound) models have also been reported using an effective mobility given by an equation similar to (3) and taking also into account bipolar trapping and recombination of carriers as well as Schottky injection at the electrode/dielectric interface [11]. The transport equations can then be numerically solved yield the current density as a function of time. It generally leads, as expected, to an increase of the number of effective charge carriers as well as their mobility resulting in a higher conductivity as the temperature increases.

To reach the highest voltage levels and transmission capacity of HVDC power cables the insulating materials must display low DC conductivity, controlled space charge accumulation together with high electrical breakdown strength. The low DC conductivity is favorable but is not the ultimate goal. The major cause of failure in HVDC systems is the accumulated space charge and its distribution is a function of the gradient of the DC conductivity in the insulation layer. The tendency to space charge accumulation is being investigated in the following section.

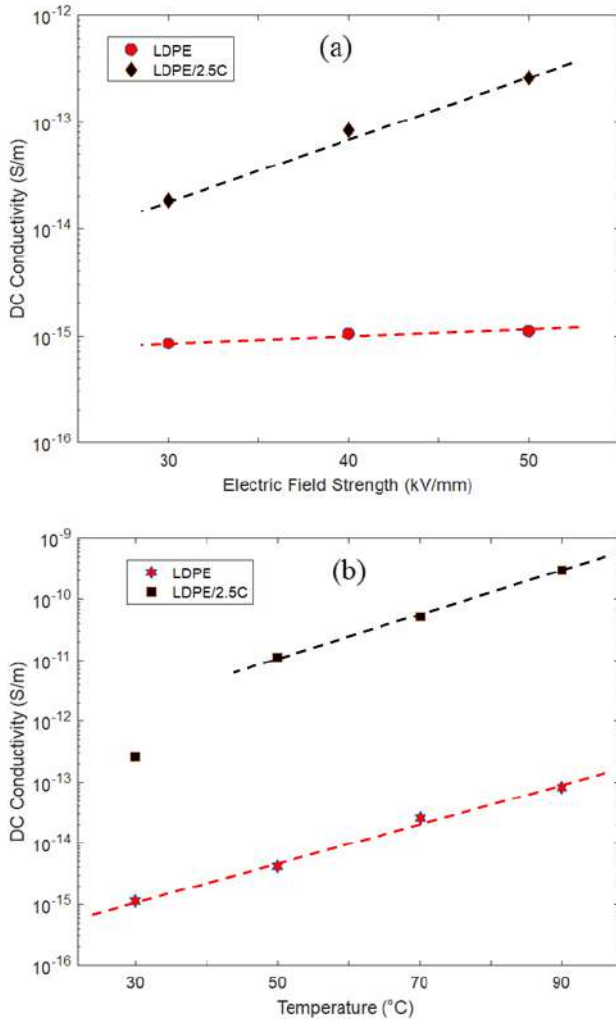


Figure 3. Effect of field variation (a) and Temperature (b) on charging currents of LDPE and LDPE/2.5C at 30 °C.

3.2 SPACE CHARGE MEASUREMENT

Figure 4 illustrates the time-dependent charge distribution profiles of LDPE and LDPE/5C under different poling fields from 10 kV/mm to 70 kV/mm at 30 °C. At the lowest applied electric field (10 kV/mm) no accumulated space charge is detected in the bulk of LDPE or LDPE/5C nanocomposite. For neat LDPE at 30 kV/mm, a packet of positive charge is injected by the HV electrode which gradually penetrates and disperses in the polymer bulk while a thin layer of negative homocharge on LV electrode builds up. For nanocomposite, however, the increase in the electric field does not appear to have more than a slight effect on the charge distribution. Indeed, only a very small heterocharge buildup close to the electrodes can be observed at the beginning of depolarization step. When the electric field goes up to 50 kV/mm, the positive charge packet leaving the HV electrode is much bigger in LDPE than at 30 kV/mm. The vast amount of injected positive charge overwhelms negative charge injected from LV electrode, thus spreading in all the insulation bulk.

Positive charge is accumulated mostly as homocharge close to the anode. When the electric field is at the highest level (70 kV/mm), a big amount of negative charge injected from the LV electrode triggers several positive charge packets which transit in the insulation bulk repeatedly during polarization step in a background of bulk negative charge. The nanocomposite sample shows the same pattern under 50 kV/mm of electric field, but with a slightly more enhanced negative charge layer in the middle. Figure 5 plots the maximum field during the polarization for LDPE and LDPE/5C at four different applied electric fields corresponding to the space charge patterns illustrated in the Figure 4. At 10 kV/mm, the field patterns almost overlap each other, very close to the applied field hinting a probable ohmic behavior. For higher applied electric fields, ohmic behavior does not hold anymore and the maximum fields are always above the applied electric fields. The deviation is bigger for neat LDPE in comparison to LDPE/5C nanocomposite and its

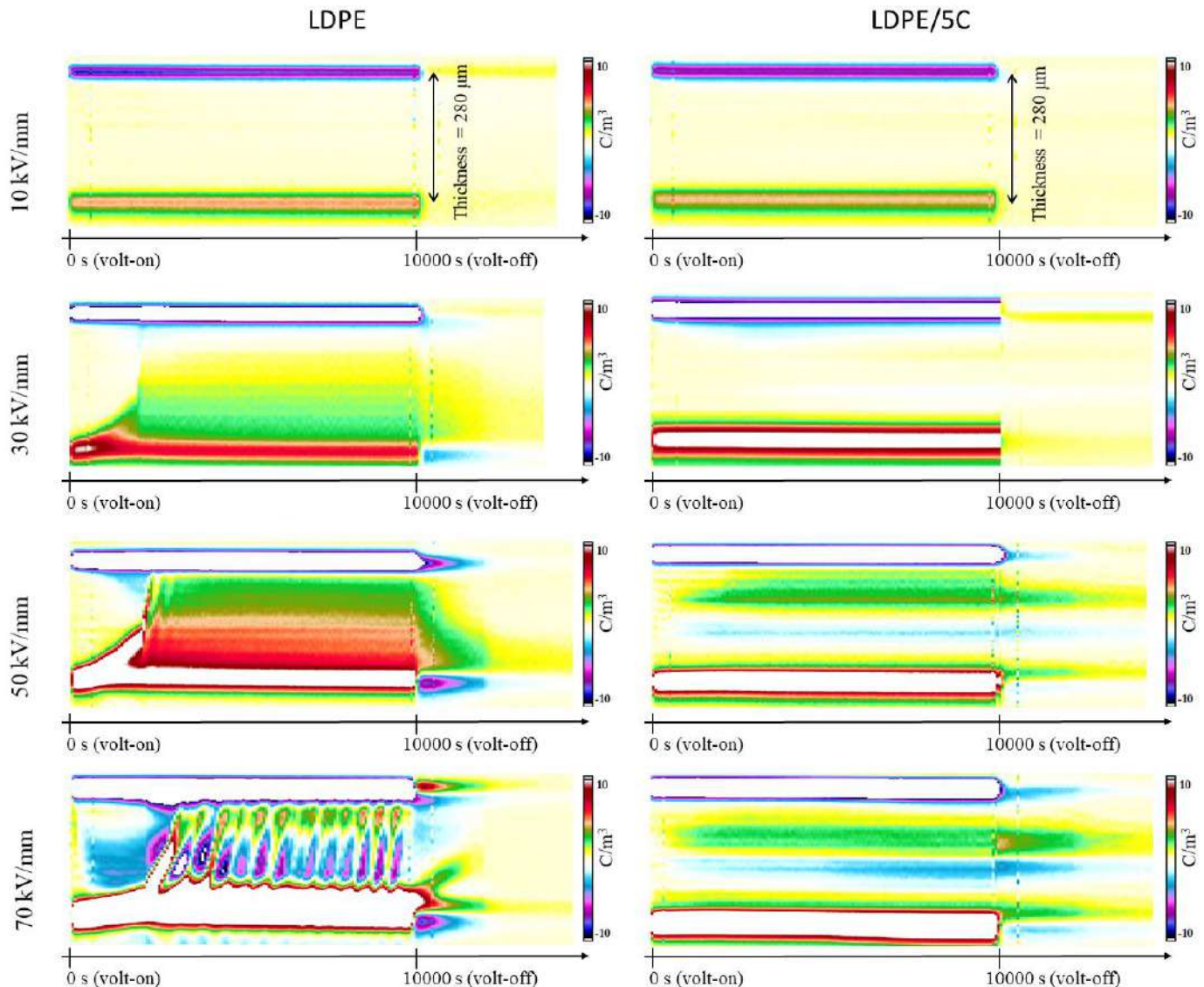


Figure 4. Space charge patterns for LDPE and LDPE/5C nanocomposites at 20 °C under different applied electric fields.

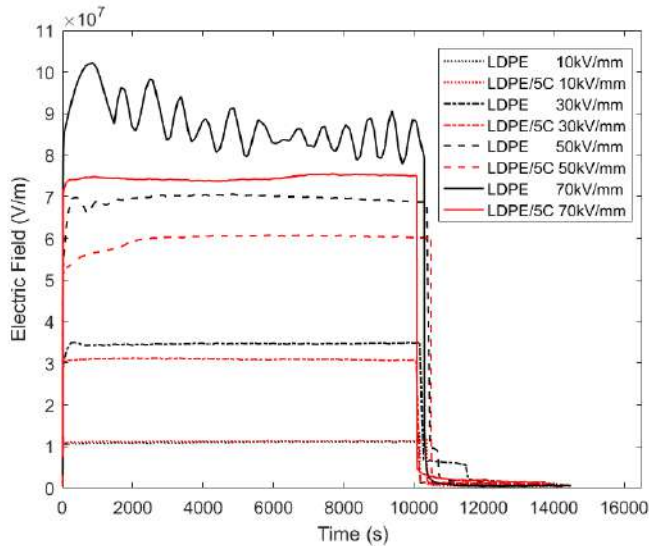


Figure 5. Maximum recorded electric field during the polarization period corresponding to the space charge patterns of Figure 4.

1 intensity increases for stronger applied electric fields at each
2 step. The heterocharge layers at each electrode are responsible
3 for this significant increase. The maximum electric field for
4 LDPE at 70 kV/mm heavily fluctuates showing a peak every
5 time a charge packet from HV electrode reaches the LV
6 electrode. It occurs, on average, every 700 seconds which can
7 be translated into a charge packet speed of about 4×10^{-7} m/s
8 considering the thickness of the LDPE sample (280 μ m).

9 Attention must be paid when interpreting the space charge
10 accumulation graphs, since at each point the net charge is
11 being displayed. The PEA signal cannot distinguish between
12 the exact amount of positive and negative charge. An area
13 with low charge level could also be due to overlapping of
14 charges having opposite polarity. Therefore, low amount of
15 detected charge in the graphs does not necessary mean that
16 there is low electrical conduction across the thickness of the
17 insulator. In fact, according to the DC conductivity results it
18 was observed that for nanocomposite, even for the lowest
19 loading of nanofiller, the conduction current level is
20 significantly higher than that of neat LDPE.

21 It appears that the increase in the DC conductivity of
22 nanocomposites allows space charge to flow across the
23 insulation wall instead of accumulating inside the insulation
24 bulk. In fact, clay seems to be effective in reducing the space
25 charge not entirely by preventing it from happening but with
26 creating a smooth passage network for charge carriers to be
27 transported away. However, it must be noted that shallow
28 traps are mostly responsible for conduction process, while the
29 incorporation of nanoclay certainly introduces a great portion
30 of deep traps, especially on the surface of nanoparticle [22].
31 The growth of interfaces of nanoparticles due to the
32 intercalation of LDPE chains increases the density of defects
33 on the surface of nanoparticles resulting in increased number
34 of localized states within the band gap of the material. This
35 will narrow the band gap and hinder the charge transport. As a
36 result, the trap density and trap depth distribution is modified.
37 Overall the presence of nanoclay facilitates the conduction

38 process by introducing more charge carriers to be transported
39 through shallow traps, while suppresses the space charge
40 accumulation by introducing deep traps. This mechanism is
41 particularly efficient at the electrode/insulation interface,
42 because it prevents the injection of excess charge from the
43 electrode at high fields. In other words, most of the charge
44 carriers crossing insulation through shallow traps are extracted
45 at the electrode while some of the electrode-injected charges
46 are immobilized in deep traps near electrodes. This explains
47 the locations of accumulated charges which are near the
48 electrodes in case of nanocomposites, but mostly appears in
49 the bulk of the unfilled LDPE.

50 Space charge patterns for LDPE and its corresponding
51 nanocomposites at elevated temperature (60 °C) under 50
52 kV/mm of applied electric fields are illustrated in Figure 6.
53 For neat LDPE a huge amount of negative charge gradually
54 appears in the whole insulation bulk, and no positive charge
55 packet was detected. Surprisingly, despite the massive
56 negative charge injected from LV electrode, it shows
57 relatively lower amount of accumulated charge than the low

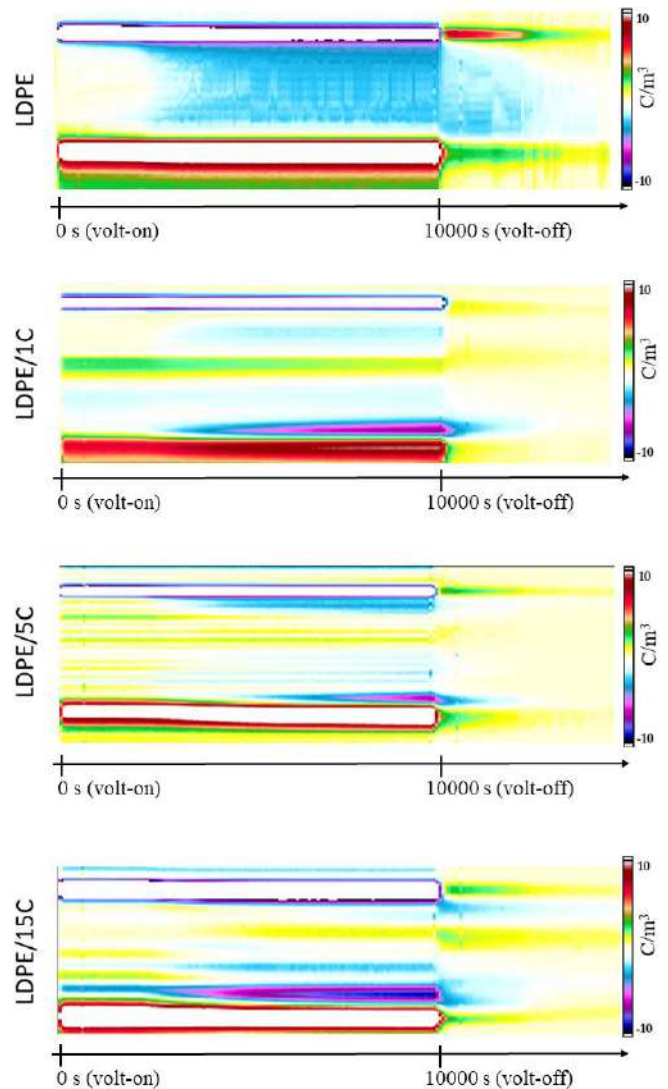


Figure 6. Space charge patterns for LDPE and its clay-containing nanocomposites at 60 °C and 50 kV/mm of applied electric field.

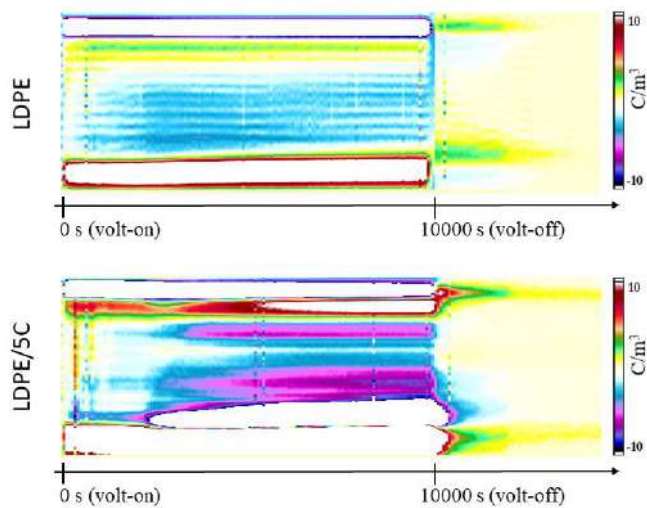


Figure 7. Space charge patterns for LDPE and LDPE/5C at 60 °C under 70 kV/mm of applied electric fields.

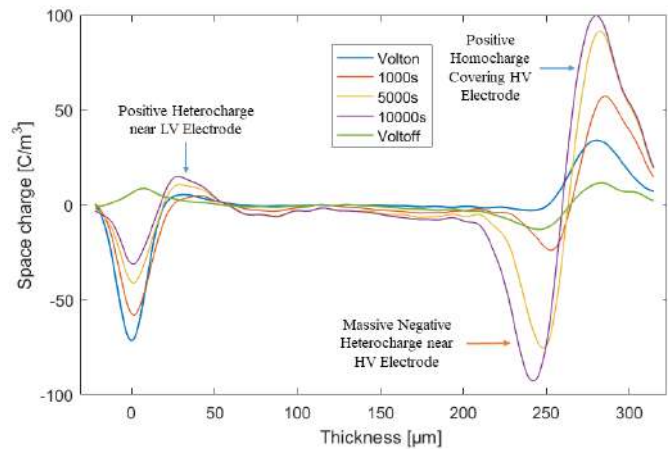


Figure 8. Space charge profile for LDPE/5C at 60 °C under 70 kV/mm applied electric field.

1 temperature pattern at the same poling field where injected
2 positive charge dominated. The domination of negative charge
3 at elevated temperature in LDPE has been recently reported
4 [23]. Space charge patterns are improved upon incorporation
5 of nanoclay at any concentration: negative heterocharge
6 gradually builds up near HV electrode while thin layers of
7 positive charge appear in the center. Negative heterocharge
8 build-up instead of dispersing in the whole specimen is
9 another sign of increased charge mobility (conductivity) where
10 negative charges manage to travel across the thickness to
11 reach HV electrode. The thermal energy provided accelerates
12 the detrapping process, combined with the electric field effect
13 induced by the trapped charge itself that allows a part of
14 trapped charges to become mobile and reach the opposite
15 electrode.

16 Space charge patterns for LDPE and LDPE/5C at elevated
17 temperature (60 °C) under 70 kV/mm of applied electric fields
18 are illustrated in Figure 7. For LDPE thin layers of
19 heterocharge are close to both electrodes while negative
20 charges are spread across the thickness of the specimen. The
21 nanocomposite sample (LDPE/5C), however, exhibits the
22 most distorted space charge behavior of all where
23 heterocharge layers being immediately built up close to both
24 electrodes. The corresponding charge profile for LDPE/5C is
25 illustrated in Figure 8 for further analysis. Charge profile
26 within the specimen is hugely affected by these heterocharge
27 layers and never reaches the steady state. While the maximum
28 electric field for LDPE never exceeds 81 kV/mm, for
29 LDPE/5C it constantly increases and reaches 180 kV/mm at
30 the end of the polarization (not shown here).

31 When combined by high poling field, elevated temperature
32 completely reverses the charge profile trend for neat LDPE
33 and its clay-containing nanocomposite. First for neat LDPE,
34 charge packet travelling across the sample were not observed
35 anymore unlike what was measure at room temperature, as
36 illustrated in Fig. 4. It seems that the increase of conductivity
37 is high enough to allow disperion of the charge packets and
38 injected charges to be drifted away but not high enough for

39 charge carrier to be massively tapped within the insulation
40 bulk. For LDPE/5C, under these temperature and field
41 conditions, the conductivity was found to reach 10^{-10} S/m,
42 which is mainly due to electronic conductivity as explained
43 previously. Due to this relatively high value (for a material
44 that is mainly non-conductive) significant heterocharge
45 accumulation occurs close to both electrodes as depicted in
46 Figures 7 and 8. This fact can be explained again considering
47 the deep traps introduced by nanoclays which prevent
48 injection but also extraction of charges. Since the activation
49 energies for both processes can be different, at high fields /
50 temperatures extraction barrier can prevail, determining a
51 significant delay for charge extraction which leads to a huge
52 heretocharge accumulation.

4 CONCLUSIONS

54 Charge transport and accumulation under high electric fields
55 were studied for neat LDPE and its clay-containing
56 nanocomposites. The incorporation of nanoclay in LDPE was
57 shown to significantly increase the DC conductivity. This
58 increase was shown to be directly related to the temperature,
59 electric field and the loading of nanofiller. The increased
60 conductivity of the nanocomposite with regard to the neat
61 LDPE together with the trapping effect of clay nanoparticles
62 was found to lead to an improvement in the mitigation process
63 of space charge at high fields and room temperature where
64 extremely low accumulation of space charge was detected for
65 nanocomposites comparing to the base polymer. However, at
66 elevated temperature the conductivity of the nanocomposites
67 reach a point ($\sim 10^{-10}$ S/m) where it doesn't provide anymore
68 benefit allowing to leak out the space charge but rather
69 enhance the space charge accumulation resulting in heavy
70 charge build up close to the electrodes.

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