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Space charge decay in low density polyethylene –montmorillonite clay multilayer nanocomposites

T. KRAUSE[1], L. MOROŃ[2], E. MOTYL[3], P. ŻYŁKA[*3]

[1]Alstom Power Sp. z o.o., Wrocław Branch, Poland

[2]Electrotechnical Institute, Division of Electrotechnology and Materials Science, Wrocław, Poland

[3]Wroclaw University of Technology, Institute of Electrical Engineering Fundamentals (I-7), Poland

The space charge accumulation and decay at low density polyethylene (LDPE)/(LDPE– montmorillonite (MMT) nanofiller composite) interfaces were investigated using the step electroacoustic (SEA) method. A three-layered specimen was polarized under dc voltage at 90 °C. After cooling under field, the short circuit currents as well as SEA signals were measured during TS discharging of the sample. The MMT nanofillers affect the electrical properties, particularly conductivity of composites and play an important role in charge distribution. LDPE/LDPE–MMT interfaces act as carrier traps and favour accumulation of charges at higher temperatures.

Key words: *LDPE insulation; nanocomposites; insulation interface; space charge dynamics; SEA technique*

1. Introduction

Polymer–clay nanocomposites are two phase materials where nanoscale inorganic particles are dispersed in an organic polymer matrix. On a nanometer level, the inorganic fillers improve the properties of the polymer. Since the nylon–clay nanocomposites with excellent mechanical properties were developed, polymer–clay interactions have been actively studied [1, 2, 3]. The most commonly used clay is montmorillonite (MMT). MMT is a crystalline, 2:1 layer clay mineral in which a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets [4]. The thickness of the platelets is of the order 1 nm and the aspect ratios are high, typically 100–1500. The molecular weight of the platelets (about 1×10^8) is considerably higher than that of typical commercial polymers. The layers are stacked one above another and the interlayers are occupied by metallic cations, usually Na^+. The silicate layers are coupled by

[*]Corresponding author, e-mail: zylka@elektryk.ie.pwr.wroc.pl

weak dipolar forces or van der Waals forces. The sheets bear charge on the surface and edges, this charge being balanced by counter ions which reside in the inner layer spacing of the clay. One important consequence of the charged nature of the clays is that they are generally highly hydrophilic species and therefore naturally incompatible with a wide range of polymer types. A necessary prerequisite for successful formation of polymer–clay nanocomposites is therefore alteration of the clay polarity to make the clay "organophyllic". It is made by ion exchange reaction. Na^+ ions residing in the interlayers can be replaced by organic cations such as alkylammonium ions, which makes organosilicates compatible to polymers. The organosilicates can be broken down into their nanoscale structures and homogenously distributed in the polymeric matrix to form exfoliated nanocomposites [5]. The exfoliated structure is the most desirable for improvements of mechanical properties, thermal stability and heat resistance. The polymer–clay nanocomposites exhibit improved tensile modulus, decreased permeability to gases, flammability reduction, chemical resistance and environmental protection [6].

Low density polyethylene (LDPE) is one of the most widely used polymers as electrical insulation. LDPE–MMT nanocomposites show improved tensile strength and modulus with good flammability resistance [7, 8]. The improved tensile strengths were observed also at 70 °C [9]. In addition to higher heat resistance and flame retardancy, the LDPE–MMT nanocomposites show the lower impermeability to gases and vapours, what can be the effect of barrier properties [10]. The electric properties of LDPE–MMT nanocomposites were rarely reported. Some results indicate that addition of nanoparticles enhances partial discharge and corona resistance and affects the conduction mechanism of nanocomposites [10–12].

In the present paper, the space charge accumulated in LDPE/LDPE–MMT/LDPE composite multilayer samples after thermoelectret polarization at higher temperature was investigated. The space charge distribution along the sample thickness was measured using step electroacoustic method. The measurements were performed during thermally stimulated discharge of the electret sample with the constant heating rate.

2. Experimental

Materials. Low density polyethylene GGNX 18-D003 (melt index 0.3 g/10 min) was used as a matrix polymer. The MMT nanofiller in the form of granular concentrate C.30.PE (50% PE + 50% MMT) was supplied by Nanocor. A suitable amount (1:7.3) of granular concentrate was added to LDPE matrix in order to obtain concentrations of 6 wt. % of MMT nanofiller. The compounds were mixed simultaneously using internal mixer of rotating single screw extruder. Test specimens were prepared by pressing at 170 °C for 1 min.

Samples. A schematic structure of a specimen is shown in Fig. 1. The thickness of the specimen was typically ca. 210 μm, consisting of 3 layers. The LDPE–MMT layer ca. 90 μm thick is placed in between two LDPE layers ca. 60 μm thick. Ag electrodes

with the diameters of 12 mm were evaporated on the sample in vacuum. The interfaces were formed by laminating pure and composite LDPE films. The layers were

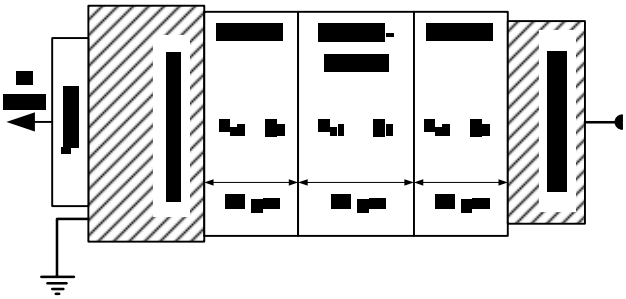

Fig. 1. Schematic diagram of a specimen

pressed firmly at 90 °C in order to avoid any cavities at interfaces. The electrical behaviour of the interfaces depends on microstructure and smoothness of the surfaces, their physical properties as well as temperature and contact pressure. That is why the sample preparation has been completed very carefully. Such three layered samples were polarized at 90 °C by 10 min under dc voltage of 2.1 kV and slowly cooled down under field to room temperature. Then the thermoelectret samples were discharged thermally at constant heating rate b = 2 K/min.

Space charge distribution method. The space charge profiles along the sample thickness were measured using a step electroacoustic system illustrated in Fig. 2.

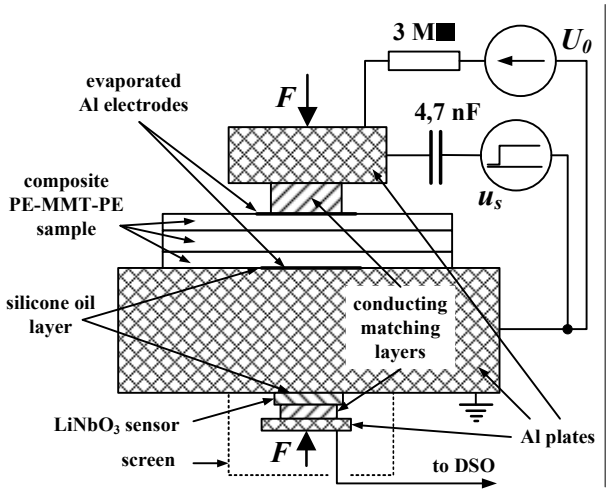

Fig. 2. Schematic SEA setup for measurement of acoustic waves

The three-layered specimen is inserted between electrodes and a step-like voltage u_s is applied to the sample to generate pressure wave. Its rise time is about 1 ns and the

amplitude is 3 kV. The bias dc voltage U_0 was applied for calibration and for measurements. The measurement system is placed in a temperature-controlled chamber with a controlled linear temperature rise. In the presented system, a 0.4 mm thick $LiNbO_3$ piezoelectric crystal was used as a transducer of acoustic waves. It enables measurements at higher temperatures to be performed.

Space charge distributions were measured under dc electrical voltage U_0 = 1.5 kV at temperature range from room to 390 K. The output signal is voltage generated in thick piezoelectric crystal by transmitting pressure wave and measured along R = 50 Ω input of DSO. In the case of the step voltage applied to the sample and thick piezoelectric sensor, the signal related to short circuit current response gives information on electric field distribution. The measured signal $u_R(t)$ is distorted by measurement circuit and should be processed in order to get information on electrical field profiles. In order to obtain quantitative information, the calibration has to be carried out. For this reason, the electric field profiles were integrated. The maximum of the integrated signal corresponds to the sum of the applied voltage u_s+U_0. The calibrated profiles of electric potential distribution for various values of U_0 are shown in Fig. 3.

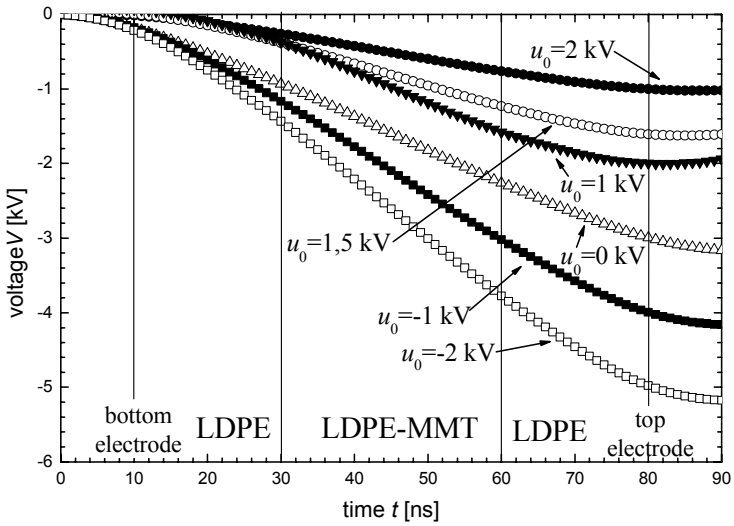

Fig. 3. Electric potential distribution obtained after integration of short circuit signals proportional to the electric field. The positions of interfaces in 3-layered specimen are marked with lines. The specimen was thermoelectrically charged under dc voltage 2.1 kV at 90 °C for 10 min, u_s = –3 kV

The calibrated profiles of the electric field and space charge distributions are obtained from the first and second derivatives and of potential profiles respectively. Location of the charge at position z can be described in terms of time because of the relation $z = vt$, when the sample acoustic wave velocity is v. Perturbation forces generated by step voltage u_s depend on internal space charges in a sample as well as on polarizing U_0 and step u_s voltages applied to the sample. The SEA measurements were per-

formed under condition $U_0 = -0.5u_s$. Under this condition, perturbation forces theoretically should not be related to external voltages and measured signal should give information on internal electrical state of charged sample [13]. It can be seen from Fig. 3 that in the case of $U_0 = -u_s$, the signal at the top electrode equals zero. This means that pressure signals from internal charges and external applied voltages are compensated. This signifies that initial potential from internal charges equals ca. 1.5 kV.

3. Results and discussion

3.1. The SEA signals

The SEA signals measured from 300 K to 375 K for the layered sample are shown in Fig. 4. It can be seen that positions of peaks are shifted in time with the increasing temperature. The shift may be the result of the thermal expansibility as well as decreasing of acoustic wave velocity in Al delay line. These changes were taken into account during interpretation of test results.

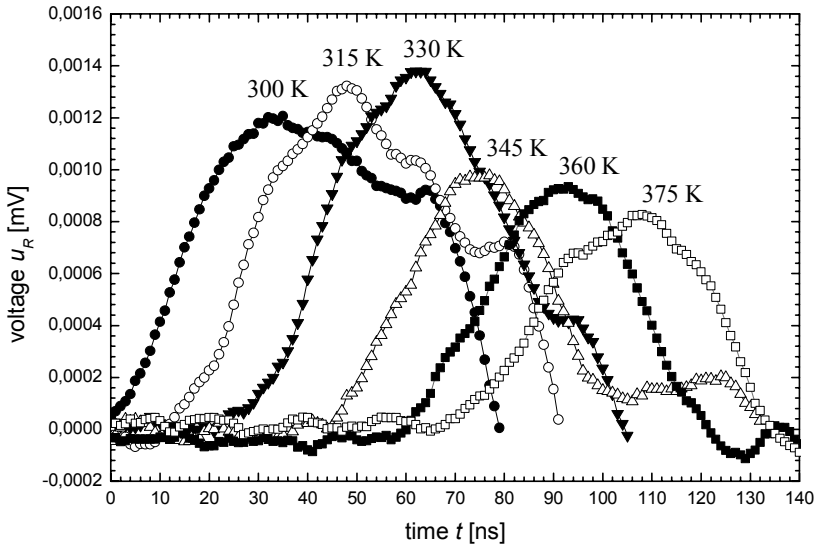

Fig. 4. SEA signals are shifted in time with the increasing of measuring temperature, ranging from 300 K to 375 K; $u_s = -3$ kV, $U_0 = 1.5$ kV

3.2. Space charge and electric field distributions

Figure 5 shows how the internal space charge distribution evolves with time during thermally stimulated discharge process. Signals from charges at electrodes related to applied voltages ($U_0 + u_s$) are not observed.

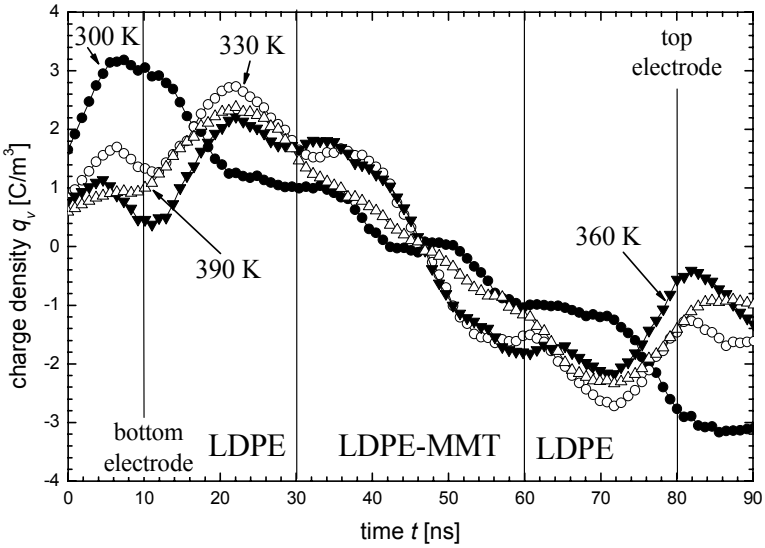

Fig. 5. Evolution of the space charge distributions during TSD at elevated temperatures. Sample polarized under 2.1 kV at 90 °C by 10 min

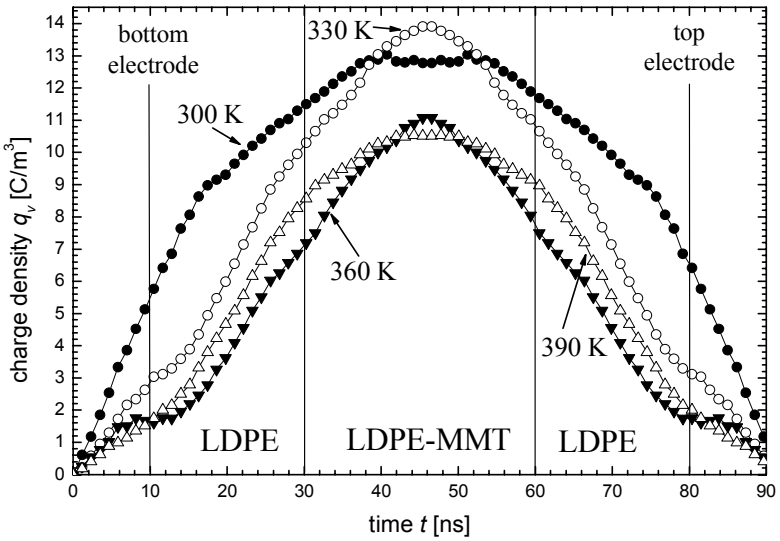

Fig. 6. Electrical field profiles along the LDPE/LDPE–MMT/LDPE composite samples during thermally stimulated discharge

Accumulated charges are heterocharges because the sign of the charge near the electrode is opposite to the electrode potential during polarization process. The heterocharges are dominant in each layer of a triple laminate specimen and in each stage of discharging. The heterocharges originate from the bulk and not from the electrodes. Various organic and inorganic impurities are the major contributor to heterocharges at

low electric field [14]. Initially (300 K) the charge accumulated near electrodes can be seen. Small space charges were observed near LDPE/LDPE–MMT interfaces. Positive heterocharges accumulated in the left LDPE layer near electrode decay during discharging and near the left LDPE/LDPE–MMT interface hetorocharge builds up. It can be observed already at 330 K on the both sides of the interface. The similar behaviour is observed near right LDPE/LDPE–MMT interface for negative heterocharges. The accumulated charges decay gradually with temperature.

Slow decay of space charge causes decreasing of the electric field mainly in the near electrode regions as it is seen in Fig. 6. The maximum electric field occurs in LDPE–MMT layer of the specimen, where the space charge density is equal to zero. It is probably the effect of charges recombination. The slow decay of space charges shows that the nanostructure of MMT generates traps and interfaces which are barriers for charge transport. Electrical properties of LDPE–MMT layer seem to have great influence on space charge distributions.

3.3. Electric characterization of LDPE layers

The measurements of electrical conductivities and permittivities of LDPE and LDPE–MMT nanocomposites were performed from 300 K to 396 K. The temperature dependences of electrical conductivities are shown in Fig. 7.

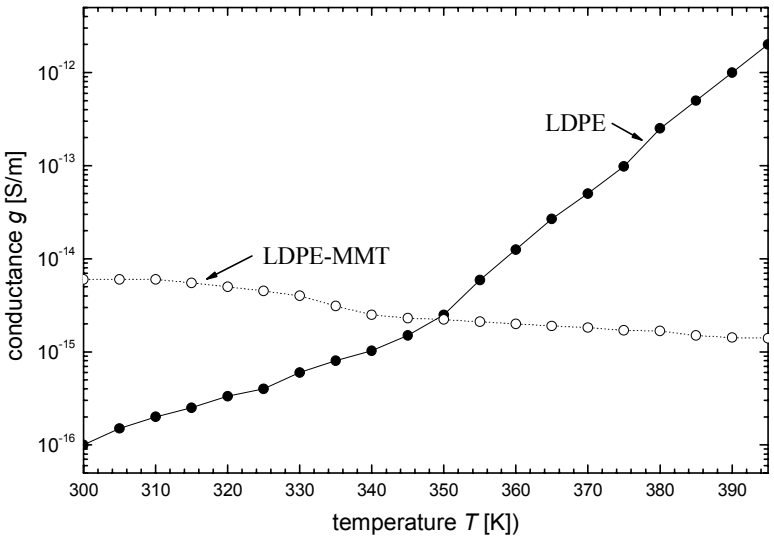

Fig. 7. The temperature dependences of conductivities of pure LDPE layer and MMT doped LDPE layer

A substantial increase of conductivity from 10^{-16} S/m to 10^{-12} S/m in LDPE is observed in the given temperature range, which is a well known phenomenon. However, in the LDPE–MMT nanocomposite, only a slight decrease of conductivity from

6×10^{-13} S/m to 2×10^{-13} S/m can be seen. It indicates that concentration of charge carriers in LDPE–MMT does not change. At low temperatures up to 350 K the conductivity of the LDPE–MMT prevails that of LDPED, while at higher temperatures, the conductivity of pure LDPE is higher than in LDPE–MMT nanocomposite. Therefore, the differences in conductivities can affect the observed changes in space charge and electric field distributions. It seems that permittivities do not affect the observed distributions very much because differences in their values are not significant as it can be seen in Fig. 8.

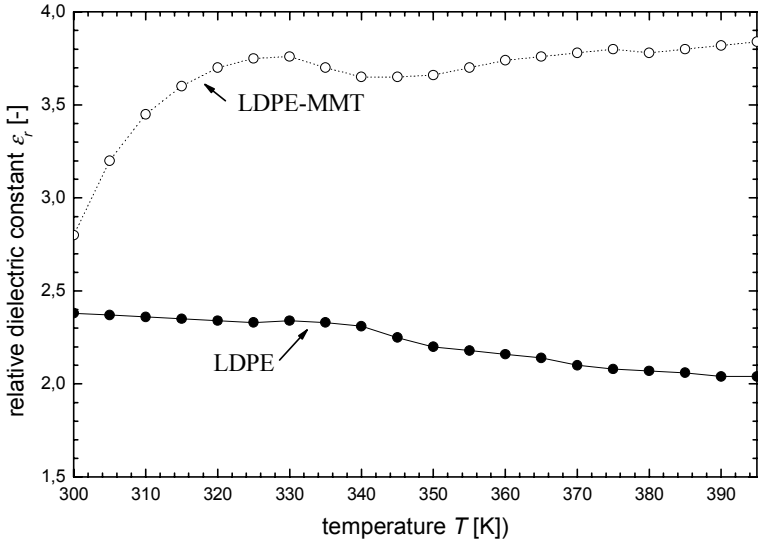

Fig. 8. The temperature runs of relative permittivities of pure LDPE and MMT doped LDPE

3.4. TSD currents

Figure 9 shows short circuit TSD current for triple layer thermoelectret sample polarized at 90 °C by 10 min under 2.1 kV and next slowly cooled to room temperature under the electric field. The thermogram shows peak at 385 K. This peak is related to decay of heterocharges in LDPE stored at near electrode regions. They may originate from low molecular mass impurities [15]. LDPE is partially polar because of organic peroxide compounds, and ketonic carbonyl groups. Such kinds of impurities could be polarized under the voltage to form heterocharges. The released charge during TSD is about 40 μC/m^2 and is similar to the change of the charge accumulated near the electrode. The measuring efficiency of various TSD processes depends on the mechanism of charge decay. The current release by dipole reorientation has the 100% efficiency. In the case of the excess charge decay by drift or conductivity, current efficiency is poor. Decay of symmetrical or antisymmetrical distributions of space charge may give no current in external circuit [16]. The distribution seen in Fig. 5 is symmetric and

great amount of charge is stored near LDPE/LDPE–MMT interfaces above 390 K. Therefore, the interfaces can act as barriers for charge migration where some charge can be trapped during polarization.

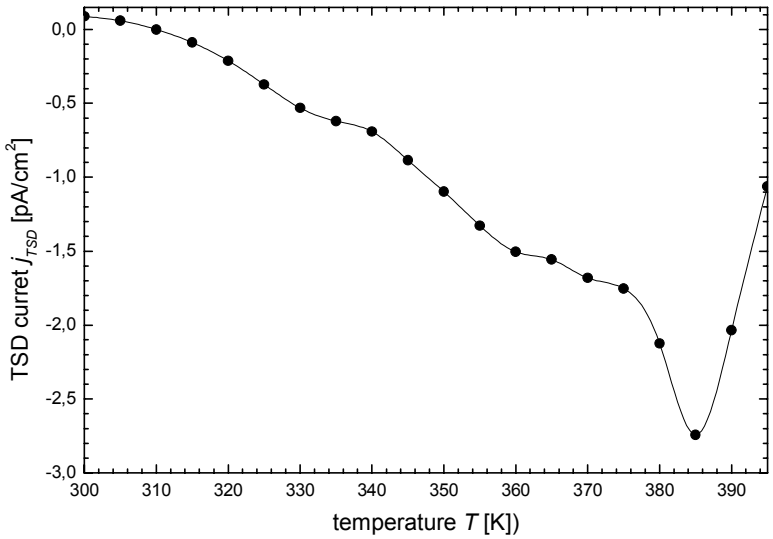

Fig. 9. Thermally stimulated discharge current of triple layer specimen. Thermoelectret sample polarized at 90 °C for 10 min under 2.1 kV

4. Conclusions

A heterocharge was accumulated at interfaces after thermoelectret polarization of triple layer LDPE/LDPE–MMT/LDPE specimens. During thermally stimulated process charge accumulated near electrodes decays first. The change of the charge accumulated near electrode is similar to the released charge during TSD. The high efficiency of decay process suggests dipole reorientation as the main discharge process. The heterocharge stored at LDPE/LDPE–MMT interfaces is very stable. Such interfaces create deep traps and barriers for charges. This phenomenon would result in the reduction of the local electric field between the electrode and the bulk.

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