The study of the charge relaxation kinetics in polyethylene with nanofillers

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Abstract. The work focuses on the study of the charge relaxation kinetics in composite materials based on polyethylene. Time dependences of the electric potential differences for samples with different mass values of the filler, as well as dependences of conductivity from the mass percentage of the filler, were achieved. The conductivity curves were analyzed according to the modern theory of intrinsic conductivity.

1. Introduction

Today one of the main focuses of the modern science is to develop new materials with upgraded performance, which can meet the rising requirements of the industry. High voltage engineering is no exception: new problems and tasks appear every day, which can be solved by creating dielectric materials with better or more suitable qualities.

This work focuses on new polyethylene-based composite materials. These composites were made to be used in heat-shrinkable cable joints of HV cables in order to reduce electrical field density. This can be done by using materials with high electrical conductivity. The conductivity of polyethylene can be improved by adding single wall carbon nanotubes (SWCN).

The objects of this study are samples of composite materials based on low-density polyethylene (LDPE). The samples were produced by the Institute of Macromolecular Compounds RAS. Two types of samples were made: discs (diameter: 20 mm, thickness: 2 mm) and films (width: 25-30 mm, thickness: 50-120 μm).

Used materials: low-density polyethylene (LDPE) Borealis 4423, single wall carbon nanotubes TUBALL™ MATRIX 801 (OCsial) (10%) mixed with wax (90%). The mass percentage of filler varies from 0% to 2%.

The samples were charged in a corona discharge. The electret surface potential has been measured by the method of the vibrating electrode with compensation in isothermal conditions. The goal of the experiment was to determine the effect of filler addition on the relaxation process.
2. Studying methods

2.1. Corona charging
The corona charging is one of the most frequently used methods of electret production [1]. It does not require expensive facilities and the process of production is relatively fast (about 1 min). Ions move from the discharge area surface of the sample, charge exchange between the surface and the ions begins. This method allows to produce electrets with homocharge. The sample is placed on a grounded electrode, the other electrode is a needle with a negative potential. A metal grid is placed between the needle and the sample. Biased by a negative potential supply, the grid limits the maximum voltage on the sample. The charging process ends with the potentials of the grid and the surface of the sample becoming equal [2]. Figure 1 shows the scheme of the charging equipment.

![Figure 1. Scheme of the charging equipment](image)

Sample surface potential reached 500 V, each sample was being charged for 60 seconds. The charge was conducted in the air at the room temperature.

2.2. Compensation method
The surface potential difference U was measured using the compensation method with a vibrating electrode. The scheme of the equipment is shown in figure 2.

![Figure 2. Scheme of the equipment for the compensation method](image)
A charged sample is placed on an electrode. The other electrode is vibrating; it is connected to the source of the compensating voltage. When the electrode is vibrating, the charge is induced on the electrode by the electric field of the sample. The signal is shown on the screen of the oscilloscope. The value of the compensating voltage should be chosen, so that the signal on the screen is 0.

2.3. Conductivity measurement
The electrical conductivity was studied in isothermal conditions at 20 °C. A picoammeter A2-4 with a two-electrode system was used. The sensitivity of the picoammeter A2-4 is $10^{15}$ A. The films were fixed in place using aluminum electrodes. The diameter of the electrodes was 15 mm. The charging currents were measured on constant voltage 10 V. Electrical field strength: $\sim 10^4 - 10^5$ V/m. The currents were measured after 5 minutes of charge.

This method was used for film samples. The scheme of the equipment is shown in figure 3.

![Scheme of the conductivity equipment for the compensation method](image)

**Figure 3.** Scheme of the conductivity equipment for the compensation method

3. Experimental data and results

3.1. Charge relaxation
Time dependences of the electric potential differences (T=90 °C) of the film samples with different mass value of SWCN (0%, 0.1%, 0.2%, 2%) are shown in figure 4.

![Time dependences of the electric potential differences (T=90 °C)](image)

**Figure 4.** Time dependences of the electric potential differences (T=90 °C) of the film samples with different mass value of SWCN (0%, 0.1%, 0.2%, 2%)
The speed of discharge of different samples can be compared using the time, when the electric potential difference of a sample reaches 50% from the initial value.

For the film samples with 0, 0.1%, 0.2% and 2% SWCN this condition was met at 40, 28, 15 and 10 seconds accordingly. The relaxation time goes down with the increase of the filler percentage.

The same experiment was conducted upon the discs. Time dependences of the electric potential differences (T=50 °C) of the disc samples with 0% and 2% SWCN are shown in figure 5.

![Figure 5](image1)

**Figure 5.** Time dependences of the electric potential differences (T=50 °C) of the disc samples with 0% and 2% SWCN

The plot suggest that the addition of the filler drastically increases the speed of the relaxation process.

Time dependences of electric potential differences (T=50 °C, T=90 °C) of the disc sample with 2% SWCN are shown in figure 6.

![Figure 6](image2)

**Figure 6.** Time dependences of the electric potential differences (T=50 °C, T=90 °C) of the disc sample with 2% SWCN
The plot shows that the speed of charge relaxation process strictly depends on the ambient temperature. If the temperature rises, the relaxation speed increases. At 90 °C the sample fully discharges 6.5 times faster than at 50 °C.

3.2. Conductivity

3.2.1. Disc samples
There are two relaxation mechanisms in polyethylene. The relaxation process can be caused by free charge carriers released from traps or by charge neutralization via dielectric’s intrinsic conductivity. These mechanisms can be working at the same time.

Assuming that the relaxation process is caused by charge neutralization via dielectric’s intrinsic conductivity, time dependences of conductivity can be achieved. Time dependences of electretic potential differences and the following formula are used [3].

\[ \gamma = -\varepsilon \varepsilon_0 \frac{dU}{U dt} \quad (1) \]

Relative dielectric permittivity \( \varepsilon = 7 \) for PE with SWCN.
Time dependences of the conductivity of the disc samples with 1% and 2% SWCN are shown in figure 7.

![Figure 7](image)

**Figure 7.** Time dependences of the conductivity (T=70 °C) of the disc samples with 1% and 2% SWCN

The plot suggests that the conductivity decreases over time, which is perfectly fine for polymeric dielectric materials. With the addition of extra SWCN the conductivity of the sample rises and the relaxation speed increases.

The curves can be divided into two segments. The first segment is a sharp drop, which can be caused by charge carriers releasing from traps. In the second segment \( \frac{dU}{dt} \) is smaller, the conductivity mainly consists of intrinsic conductivity [4].

The form of the curves stays the same with the addition of the filler at different temperatures. This means that the relaxation mechanisms do not change in different conditions.
3.2.2 Film samples

The dependences of conductivity from the mass percentage of SWCN are shown in figure 8.

![Graph showing conductivity vs mass percentage of SWCN]

**Figure 8.** The dependences of conductivity from the mass percentage of SWCN

Figure 8 shows that the conductivity rises from $1\times10^{-16}$ to $1\times10^{-14}$ S/m with the addition of the filler (from 0.1% to 2%). “h” is the thickness of the film.

| Vol SWCN (%) | h (μm) | \(\gamma\) (S/m, \(10^{-16}\)) |
|--------------|--------|-------------------------------|
| 0.1          | 152    | 4.54                          |
| 0.2          | 130    | 25.9                          |
| 1            | 80     | 43                            |
| 2            | 125    | 111                           |

**Table 1.** Conductivity values

4. Conclusion

As a result, time dependences of electretic potential differences and conductivity were achieved for samples with SWCN. The speed of the relaxation process and the conductivity of the sample rises with the addition of SWCN filler. The relaxation process also depends on the ambient temperature: a higher temperature speeds up the discharge.

Based on achieved data, composites with suitable qualities can be produced by varying the percentage of the filler.

References

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