1. Bożena ŁOWKIS, 2. Jan ZIAJA, 3. Aleksandra Anna KRAFT

Politechnika Wrocławska, Katedra Podstaw Elektrotechniki i Elektrotechnologii (1,2)
ORCID: 1. 0000-00022- 4702-06696 2. 0000-0002-7340-6509.

doi:10.15199/48.2023.01.11

The influence of the electrode material on the dielectric properties of PET films

***Abstract**. This paper presents the influence of the measuring electrode material on the dielectric properties of polyethylene terephthalate. We show that volume resistivity, surface resistivity, relative permittivity and the dielectric loss factor of PET films are a function of the electrode material used. We also evaluate the effect of thermal aging on the tested material parameters.*

Streszczenie.** Przedstawiono wpływ materiału elektrod pomiarowych na właściwości dielektryczne politereftalanu etylenu. Stwierdzono, że rezystywność skrośna, rezystywność powierzchniowa, względna przenikalność elektryczna oraz współczynnik strat dielektrycznych folii PET są funkcją zastosowanego materiału elektrod. Oceniono wpływ starzenia termicznego na badane parametry materiałowe **(Wpływ materiału elektrod na właściwości dielektryczne folii PET).

Słowa kluczowe: PET, magnetronowe rozpylanie, właściwości dielektryczne, starzenie cieplne.
Keywords: PET, magnetron sputtering, dielectric properties, thermal aging.

Introduction

Polyethylene terephthalate (PET) is one of the most recognizable plastics. This polymer, due to its high chemical, mechanical and thermal resistance (up to the melting point) is employed in numerous industrial areas. PET is also considered as an exceptionally environment-friendly material.

Dielectric properties of polymers are strongly connected with their structure. Recognizing electrical properties of polymeric materials [1-6] enables their responsible application as e.g. an electro-insulating material. Determination of material parameters of dielectrics, especially the electric ones, is very ambiguous. The question, how the electrode material and the method of its deposition on polymer influences the results of investigations of such parameters as resistivity, relative permittivity or dielectric loss factor, has not been resolved yet [7].

The aim of this paper was to assess the effect of measuring electrodes material on the values of dielectric parameters of a PET foil. The electrodes were made of high purity materials: Al (99,99%), Cu (99,50% and Ti (99,99%). Volume resistance R_v versus time, surface resistance R_s as a function of measuring voltage, capacity C and dielectric loss factor tan delta versus frequency were measured on a specially prepared capacitor. From the measurement results, the parameters such as volume resistivity ρ_v, surface resistivity ρ_s as well as relative permittivity ε_r and dielectric loss factor tan delta were determined. The effect of thermal aging on the material parameters has also been considered in this work.

The electrical properties were measured on a PET foil with thickness of 0.025 mm. The polymeric foil with a serial number JM-010-2018 was made in Waterford, Ireland by PPI ADHESIVE PRODUCTS. For electrodes deposition, magnetron sputtering method [8] was employed. This method has many advantages over the other ones [9]:
- possibility of deposition of well adhering conductive films with an uniform thickness,
- low temperature of film deposition, what makes that the material is not exposed to damage.

Parameters of the magnetron sputtering process have been collected in Table 1. As a working gas, Argon was used. The value of pressure in the working chamber and sputtering time (10 min.) were the common parameters for sputtering of all three metals. Due to low thickness of the foil, the sputtering was performed with 30 seconds breaks, i.e. 5 min.–30 s break–5 min. It allowed us to reduce the effect of temperature and ion bombardment on material deformation and its damage [9].

Table 1**.** Parameters of magnetron sputtering process

Parameter	**Al**	**Ti**	**Cu**
Working gas	Ar	Ar	Ar
Frequency of working gas ejection [Hz]	2.56	6.66	2.66
Sputtering time [min.]	2x5	2x5	2x5
Magnetron supply power [kW]	1.25	1.26	0.45
Reverse power [W]	20	50	10
Plasma current [A]	7	2.5	2.7
Working pressure [Tr]	$3.9\cdot10^{-4}$	$3.9\cdot10^{-4}$	$3.9\cdot10^{-4}$

According to the requirements of the Standard PN-88/E-04405 [10], the studied samples have been prepared in a three-electrode system. Microscopic pictures of cross-sections of the foils with deposited electrodes of Al, Ti and Cu are shown in Figure 1. The microscopic investigations were carried out by Nanores Ltd. using scanning electron microscopy (SEM).

Looking at Figure 1 it can be stated that the electrodes deposited on the foil are not of the same thickness; they are 133.1 nm, 119.0 nm and 110.4 nm for Cu, Al and Ti, respectively. Transition layers for the particular metals are 6.419 nm for Cu, 10.49 nm for Ti and 15.41 nm for Al.

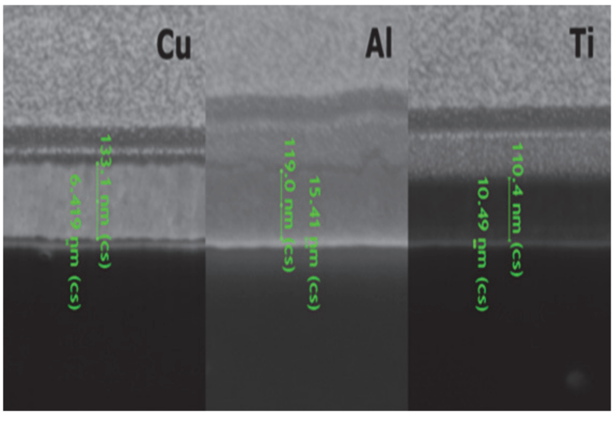

Fig.1. Cross sections of the PET foil with deposited Cu, Al and Ti electrodes

Estimation of material parameters of the PET foil

In order to estimate material parameters such as volume resistivity, surface resistivity, relative permittivity and dielectric loss factor, volume resistance, surface resistance, capacity and dielectric loss factor of the capacitors in a three-electrode system have been measured. For the investigation, three groups of samples, differing with the kind of electrode material, Al, Ti and Cu, deposited on the PET foil were used. Measurements of resistance were carried out according to the standard PN-88/E-04405 [10]. Volume resistance of the samples was measured as a function of time at two values of measuring voltage – 50 V and 100 V. Surface resistivity was measured at the voltages of 10 V, 50 V and 100 V. Measurements of capacity and dielectric loss factor of the capacitors were performed in the frequency range of 20 Hz to 200 kHz with the use of Hameg LCR bridge 8118. Characteristics of current versus time up to 1000 s at a constant measuring voltage of 100 V for the samples from each group are shown in Figure 2.

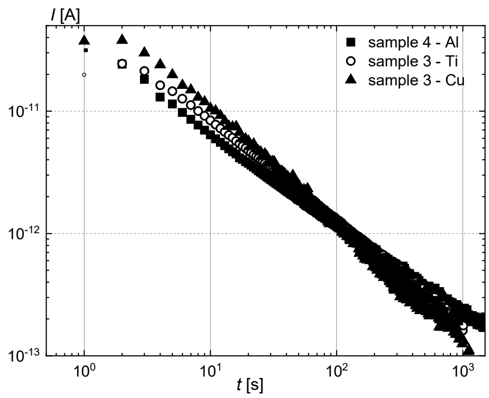

Fig.2. Current versus time at a constant measuring voltage of 100 V for the samples selected from each group

From the current measurements, volume resistivity ρ_v of the PET foil has been estimated using the equation given in [7]:

$$\rho_v = \pi \cdot R_v \cdot \frac{(d_1+g)^2}{4 \cdot h} \tag{1}$$

where: R_v – volume resistance [Ω], d_1 – diameter of measuring electrode [m], g – distance between the measuring electrode and the protective ring, h – sample thickness [m].

Volume resistivity, estimated from equation (1) versus time ρ_v=f(t) for selected samples from each group, has been shown in Figure 3.

Taking into account the surface resistance and the measuring electrodes dimensions, the surface resistivity has been evaluated, according to the equation (2) [7]:

$$\rho_s = R_s \cdot \frac{2,74}{log\frac{d_2}{d_1}} \tag{2}$$

where: R_s – surface resistance [Ω], d_1 – diameter of measuring electrode [m], d_2 – inner diameter of protective electrode [m].

Results of the measurements do not show any dependence between the value of surface resistivity and the electrode material. The surface resistivity of all samples with Al and Ti electrodes raised with the increase in the measuring voltage from 1x10^{15} Ω to 1×10^{16} Ω. Using Cu electrodes caused that the value of this parameter changed in a slightly wider range from 3×10^{14} to 3×10^{16} Ω.

From the measured capacity of the capacitors, relative permittivity of the polyethylene terephthalate has been estimated. Dependences of the dielectric loss factor and relative permittivity in function of frequency for the samples selected from each group have been shown in Figure 4 and 5, respectively.

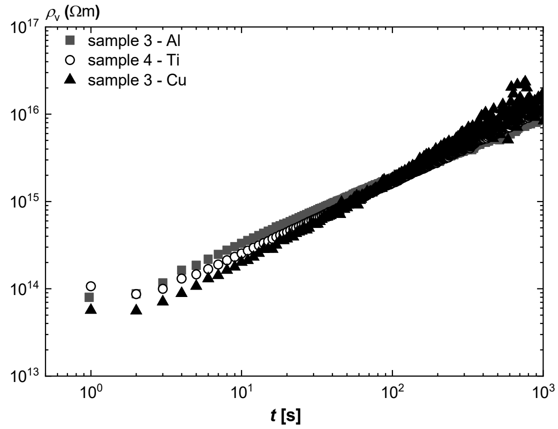

Fig.3. Volume resistivity versus time at a constant measuring voltage of 100 V for the samples selected from each group

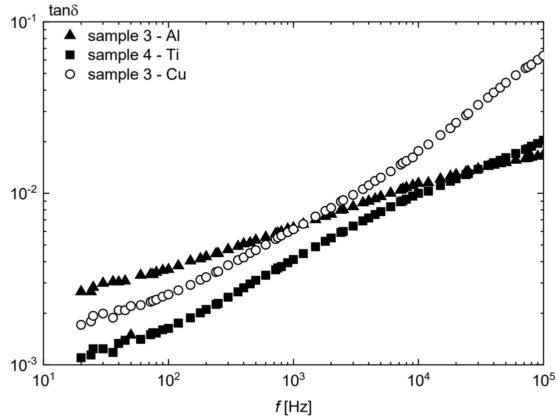

Fig.4. Dielectric loss factor versus frequency for the samples selected from each group

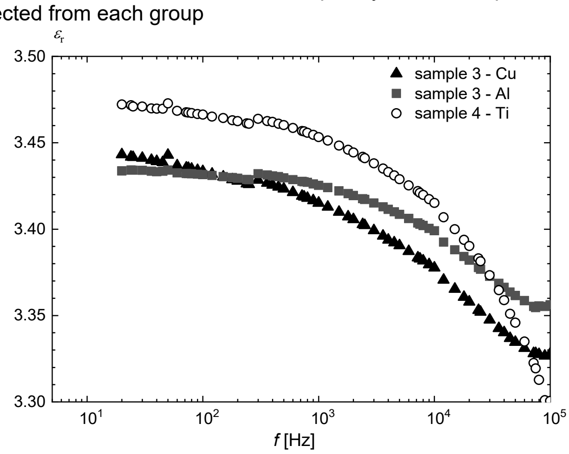

Fig.5. Relative permittivity versus frequency for the samples selected from each group

Thermal aging

Polymers are materials particularly exposed to the effect of high temperature. They commonly undergo irreversible aging processes, which results in the change of their physical and chemical properties. Consequently, it comes to breaking of chains or crosslinking of polymer microparticles, which results in the change of degree of crystallinity of the polymers [3, 4]. For research purposes, the samples of PET foil with deposited electrodes were placed for 48 h in a climatic chamber at a constant temperature of 80°C and 55% humidity. The results of investigation of material parameters of the samples with Al, Cu and Ti electrodes, including volume resistivity, surface resistivity, relative permittivity and dielectric loss factor after the aging process are shown in Figures 6–8. In Figure 6, the value of volume resistivity in function of time at a measuring voltage of 100 V has been given.

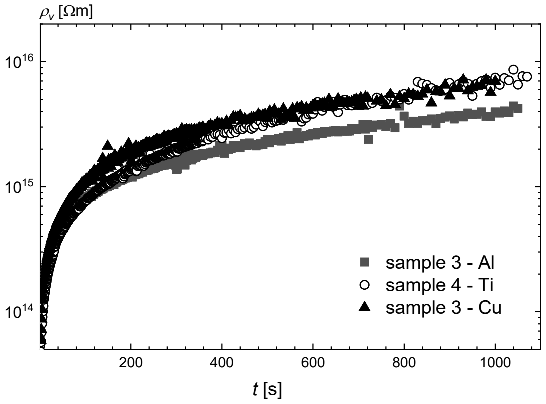

Fig.6. Volume resistivity versus time at the constant measuring voltage of 100 V for the aged samples selected from each group

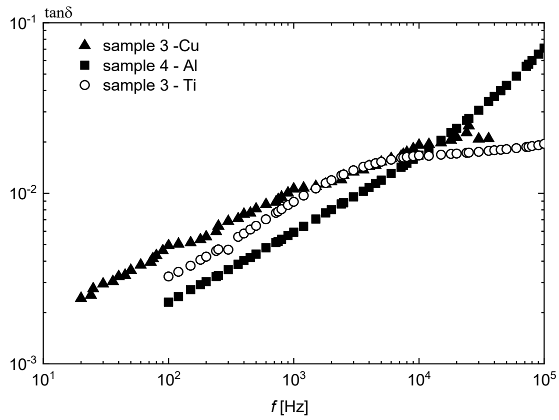

Fig.7. Dielectric loss factor versus frequency for the aged samples selected from each group

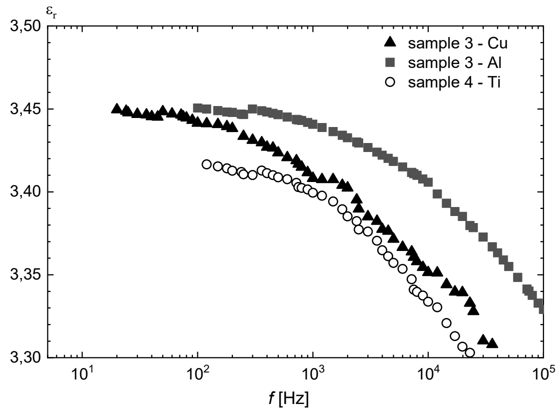

Fig.8. Relative permittivity versus frequency for the aged samples selected from each group

In Figures 7 and 8, dielectric loss factor and relative permittivity versus frequency for the samples selected from each group have been shown. It has been stated that the thermal aging process did not cause any essential change in the values of surface resistivity of the aged samples in comparison to the non-aged ones.

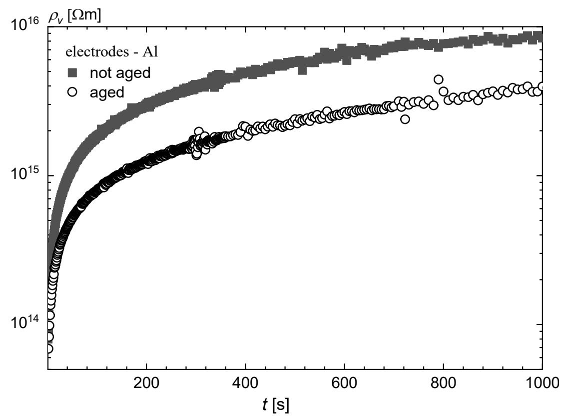

Fig.9. Volume resistivity versus time at a constant measuring voltage of 100 V for the aged and non-aged PET foil with Al electrodes

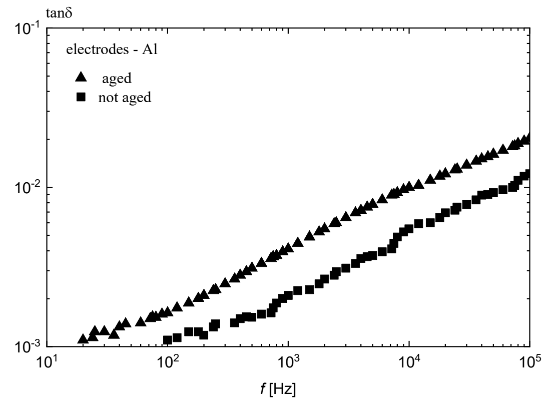

Fig.10. Dielectric loss factor versus frequency for the aged and non-aged PET foil with Al electrodes

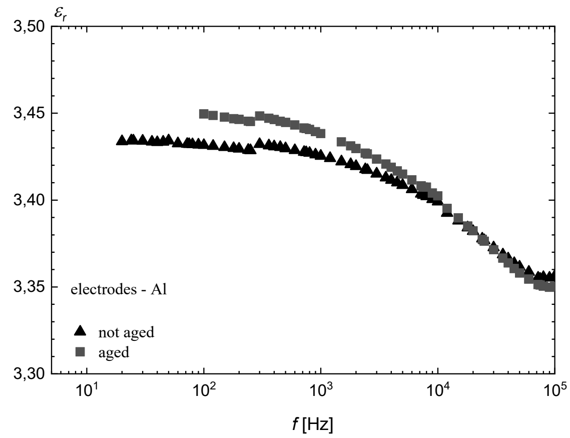

Fig.11. Relative permittivity versus frequency for the aged and non-aged PET foil with Al electrodes

Parameters of non-aged and aged PET foils

To follow the effect of aging process on the material parameters of the PET foil, dependences of volume resistivity versus time along with the dielectric loss factor and relative permittivity versus frequency for the aged and non-aged samples have been collected in the following figures. In Figure 9, the effect of aging process on the volume resistivity of the PET samples with Al electrodes has been shown. Similar dependences have been obtained for the samples with Ti and Cu electrodes. Dependences of dielectric loss factor and relative permittivity versus frequency for the aged and non-aged samples with Al electrodes have been shown in Figure 10 and 11, respectively.

Conclusions

Results of investigations on the effect of measuring electrode material and thermal aging process of PET foil on the values of material parameters, such as volume resistivity, surface resistivity relative permittivity or dielectric loss factor have been presented in this paper. It has been stated that:

1. The material of measuring electrode affects the measurement results of dielectric parameters.
2. Thermal aging process leads to the changes in values of material parameters.
3. Volume resistivity of a PET foil after aging has lower value than the corresponding value of a non-aged foil. Comparison of the characteristics of volume resistivity versus time measured for the thermally aged samples at a constant voltage showed that the lowest value of volume resistivity was obtained for the sample with Al electrodes whereas the highest one was achieved for the samples with Cu electrodes.
4. The characteristics of volume resistivity versus time, measured at a constant voltage of 50 V and 100 V, respectively show that the polarization processes are maintained up to 1000 s. The trend occurs for both aged and non-aged samples, independent of the employed electrode material (Figure 9).
5. No correlation between the surface resistivity value and electrode material has been found. The thermal aging process also has not affected the surface resistivity.
6. The dielectric loss factor increases with an increase in frequency. The values of dielectric loss factor for an aged foil are higher than the ones for a non-aged foil (Figure 10), which is particularly noticeable in case of the samples with Al and Cu electrodes. Actually, the aging process does not affect the tan delta of the samples with Ti electrodes. The dielectric losses occurring both in the aged and non-aged foils are of polarization type.
7. The values of relative permittivity depend both on the aging process and electrode material. The aging process of the samples with Cu and Ti electrodes caused some reduction of ε_r value. The tendency has not been observed in the case of aging of the foil with Al electrodes (Figure 11) where the value of ε_r was higher than that for the non-aged foil up to 10^4 Hz. Above this frequency, the effect of aging was similar to that observed for the foil with Cu or Ti electrodes.
8. Relative permittivity is a decreasing function of frequency. It means that with an increase of frequency, the value of ε_r for a polar PET foil decreases after reaching a limit value of frequency to a value depending only on electronic and ionic polarization.
9. The factors responsible for the differences in the values of the parameters determined for different electrode materials are the mass number of the metals used for the electrodes and the parameters of magnetron sputtering process. The value of "real" foil thickness which is not penetrated by the ions of electrode material depends on the depth of penetration of metal atoms. The differences in the values of material parameters of the foils with the electrodes made from different metals result from the lack of the possibility of assessment of "real" foil thickness, which may have an essential effect on computing these values and which, in fact, has not been determined.
10. The studies performed in this work require continuation in order to assess the relationships between the parameters of sputtering process and the depth of atoms penetration. For knowing the "real" foil thickness, microstructural studies are necessary.
11. On the basis of these investigations it can be stated that the PET foil has good electro-insulating properties. The differences in the values of the parameters obtained for the foils with different electrode materials and after aging process do not have a particular effect on the application in engineering practice but should be a basis for considerations of a scientific character.

Acknowledgment

This work has been accomplished within the grant No K38W05D02 – 8201003902 supporting research activities

***Authors**: dr hab. inż. Jan Ziaja, Politechnika Wrocławska, Katedra Podstaw Elektrotechniki i Elektrotechnologii, ul. Wybrzeże Wyspiańskiego 27, 50-377 Wrocław, E-mail: jan.ziaja@pwr.edu.pl, dr hab. inż. Bożena Łowkis, Politechnika Wrocławska, Katedra Podstaw Elektrotechniki i Elektrotechnologii, ul. Wybrzeże Wyspiańskiego 27, 50-377 Wrocław, E-mail: bozena.lowkis@pwr.edu.pl*

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