

NON-CONTACT DIELECTRIC MEASUREMENTS ON POLYMER FILMS

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Abstract: Dielectric characterization of materials in the RF domain is usually carried out on samples with applied electroconductive electrodes. A high-quality contact between a sample and the measuring electrodes provides a stable current flow through the sample and information on the exact value of the electric field in which the sample is located. It also enables a simple measuring instrument to determine the dielectric parameters of the material being tested. However, the presence of contact potentials and the exchange of charge between the test material and the applied electrodes can mask some electrical phenomena in the material or significantly affect how we perceive these phenomena. In order to detect weak electrical processes in the material, for example the photoelectric response of non-polar polymers, contactless dielectric measurements must be carried out. The literature on non-contact dielectric measurements in the RF domain is poor, and because of that, this paper presents the methodology for determining the dielectric parameters of film-shaped materials in conditions of contactless dielectric measurements.

Keywords: electrical measurements; contactless; polymer; charge mobility.

1. INTRODUCTION

The development of new scientific knowledge and the advancement of experimental methodology are processes that stimulate each other. The significant progress in the development of organic photocells over the past 10 years has been achieved primarily as a result of the use of complex organic composites [1–4]. Development trends in this scientific field suggest that organic photocells made of non-toxic materials will find a place in the market soon and become a serious competition for photocells based on conventional semiconductors [2,5]. Scientific studies primarily give descriptions of organic photovoltaic solutions and their functionality. On the other hand, one can notice the lack of a deeper understanding of photoelectric processes in materials from which organic photocells are made.

An organic photocell is usually comprised of more than two layers of complex composite

materials [1,6,7]. In order to improve or predict the properties of organic photocells, it is necessary to know the photodielectric behavior of each of the materials used, as well as contact interactions in the light/dark conditions between those materials. At this point, scientific articles about organic photovoltaic systems described together with the complete photodielectric characterization of the used materials could not be found. The main reason for this is the very low photoelectric response of most organic materials, i.e. experimental difficulties in its detection. The presence of electrically conductive measuring electrodes on a material can mask the electrical processes in the material due to charge exchange between the material being tested and the electrodes. In addition, the contact potentials between the electrodes and the sample affect the electrical response of the material [8–10]. Bearing in mind that there is not a standardized or widely accepted methodology of non-contact dielectric characterization of materials in the RF frequency

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domain, this paper describes an exact method of determining the dielectric parameters of the film-shaped materials in the conditions of contactless dielectric measurements. As an example of the success of the proposed method, the paper describes the change in the nature of the photodielectric response of a thin film of LDPE (low-density polyethylene) in the presence of a very small amount of graphite applied to one side of the film. This result is obtained in the contactless measurement mode, and it is practically impossible to notice if the electro-conductive electrodes are present on the sample.

2. METHODOLOGY

Schematic representation of the contact mode of the electrical measurements is shown in Figure 1a. In the case of contact measurements, the contact surface of the sample can be coated with an electro-conductive paste, soft graphite, or metal [9]. The prepared contact surfaces of the sample are brought into contact with the measuring electrodes (Figure 1a). Contactless electrical measurements are carried out in such a way that the sample is in the electric field produced by the electrodes, and there is air or vacuum between the sample and the electrodes (Figure 1b).

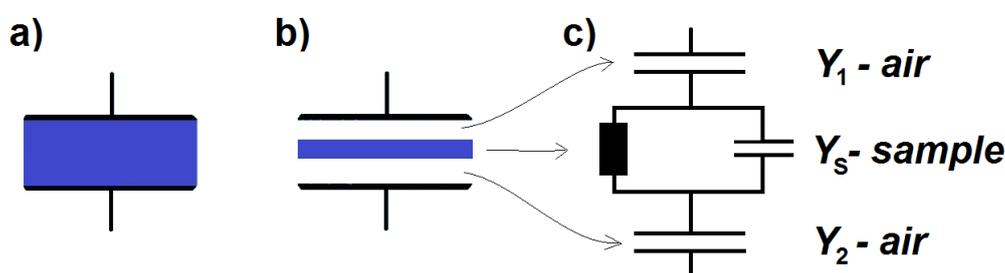


Figure 1. a) Contact and b) contactless electrical measurements, c) an equivalent RC circuit for contactless AC electrical measurements

In Figure 1c, the sample is represented as a parallel connection of the resistor and the capacitor, which is normal during dielectric measurements (Cp mode of an RCL meter). The sample model formed as a serial connection of the resistor and the capacitor (Cs mod) or more complicated is rarely used. The model shown in Figure 1c, which describes the air-sample-air system, is exact in contrast to the approximate methods of contactless dielectric characterization that can be found in the literature [11,12]. A calculation method of the dielectric parameters of the materials will be introduced in the formalism of AC electrical conductivity, Y – admittance. If the sinusoidal shape of the voltage is applied, usually for dielectric measurements, which is the case here, the admittance (AC conductivity) of the sample can be represented as $Y_S = G_S + iB_S$, G_S – conductance (in phase conductivity), B_S – susceptance (out of phase – capacitive conductivity). The susceptance is related to the dielectric permittivity of the material in the following manner: $B_S = 2\pi f C_S = 2\pi f \epsilon' \epsilon_0 S/d$, f – frequency, C_S – capacity of the sample, ϵ' – dielectric permittivity of the sample, ϵ_0 – vacuum dielectric permittivity and S/d – surface/thickness ratio of the sample. The specific values of the AC conductivity components of the material (G_{spec} and

B_{spec}) are calculated by multiplying the results obtained from the measurement (G_S and B_S) with a geometric sample factor (d/S).

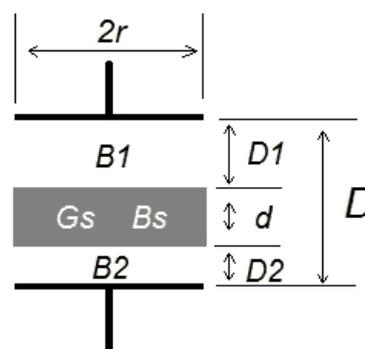


Figure 2. Measurement geometry, D - distance between electrodes, d - thickness of the sample and $2r$ - diameter of the sample and the electrodes (circular shape, $S = r^2\pi$)

The admittance of the air-sample-air system (Y), which is inside the measuring cell (Figure 1c and Figure 2) can be related to the sample admittance (Y_S) by Equation 1.

$$Y^{-1} = Y_1^{-1} + Y_S^{-1} + Y_2^{-1}, \quad (1)$$

where $Y_S = G_S + iB_S$ and $Y_{1/2} = iB_{1/2} = 2\pi f \epsilon_0 S/D_{1/2}$ (Figure 2).

In order to obtain the admittance of the air-sample-air system ($Y = G + iB$), it is necessary to perform a correction of the measurement results in relation to the measuring system and the empty cell. The use of electrical conductivity, instead of electrical resistance, in this analysis allows simple measurement corrections. It is necessary to measure the conductance and susceptance of the empty cell (G_{empty} and B_{empty}), then to perform the same measurements with a sample placed in the cell (G_m and B_m), and the components of the admittance of the air-sample-air system are $G = G_m - G_{empty}$ and $B = B_m - (B_{empty} - 2\pi f\epsilon_0 S/D)$. Knowledge of the conductance and susceptance of the air-sample-air system according to the model in Figure 1c (Eq 1), G and B , enables solving Equation 1 and obtaining the conductance and susceptance of the sample. The solutions are shown in Equations 2 and 3.

$$G_S = \frac{G}{k^2 + a^2 G^2}; \quad (2)$$

$$B_S = \frac{1}{a} \left[\frac{k}{k^2 + a^2 G^2} - 1 \right]; a = \frac{1}{E_1} + \frac{1}{E_2}; k = 1 - aB \quad (3)$$

Equation 4 shows the dependence between the amplitude of the voltage on the sample, U_s , and the amplitude of the voltage on the electrodes, U_e .

$$U_S = \frac{\sqrt{G^2 + B^2}}{\sqrt{G_S^2 + B_S^2}} U_e. \quad (4)$$

The non-contact dielectric characterization of materials exhibiting a high electrical conductivity leads to an accumulation of the charge at the sample boundaries in the direction of the electric field. This phenomenon can be seen in the frequency spectra as

an increase in susceptance (capacitance) and a decrease in the conductance at lower frequencies. On the other hand, the same phenomenon can be used to determine the mobility of the charge carriers in the tested material. Using the boundary frequency at which this process appears or disappears (f_o) during contactless measurements, with the known electric field on the sample (E) and the thickness of the sample (d), the mobility of the charge (μ) can be approximately determined by Equation 5 [13]. In this equation, the speed of the charge (v) is obtained assuming that the mean free path of the charge is equal to half the sample thickness ($d/2$) and the mean time of the charge trip is half the time of the changes in the electric field, $T/2 = 1/(2f_o)$.

$$\mu = \frac{v}{E} = \frac{df_t}{E}. \quad (5)$$

3. EXAMPLES OF THE MEASUREMENT

In order to verify the proposed methodology, measurements were made on films of different polymers. The non-contact dielectric measurement methodology outlined in this paper provides results that are similar to the results obtained in the contact measurement mode, although the dielectric permittivity and the conductance obtained by the contactless measurement were always somewhat lower than the corresponding values obtained in the contact mode. An example of the above is shown in Figure 3, which shows the results of measurements on poly(methyl methacrylate) (PMMA) films of different thicknesses.

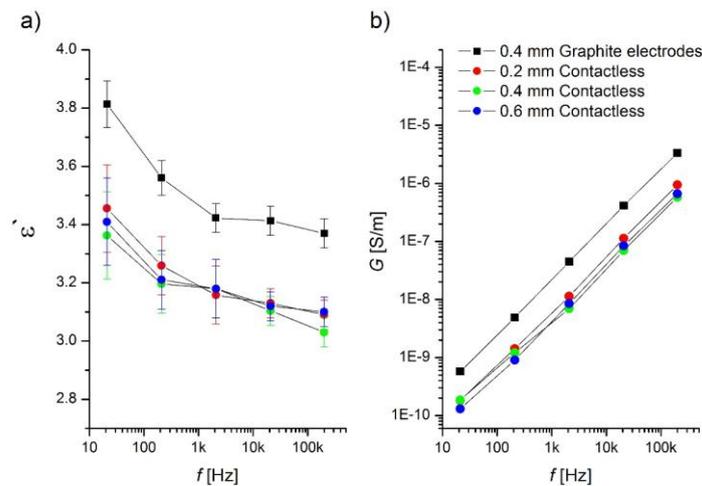


Figure 3. Dielectric parameters of PMMA films, a) dielectric permittivity and b) conductance

Bearing in mind that there are no similar results in the literature, it can be assumed that the absence of exchange of the charge between the

electrodes and the tested material is the reason for the lower values of the AC conductivity components obtained in the contactless measurement relative to

the corresponding values obtained in the contact measurement mode.

Figure 4 shows the photodielectric response of thin LDPE films measured in the contactless measurement mode, circle (red) symbols for neat LDPE film and square (black) symbols for LDPE coated on one side with a very thin (transparent) graphite layer. The relative changes in dielectric permittivity of LDPE due to illumination (white light, $P = 0.1 \text{ mW/m}^2$, red circle symbols in Figure 4) show an approximately linear increase in permittivity with time of illumination, which suggests that the increase in dielectric permittivity is due to the warming of the sample during illumination. After illumination, $t > 50 \text{ s}$ in Figure 4, the LDPE film shows a slow decrease in the dielectric permittivity, which can be attributed to

the cooling of the sample. The presence of a very thin and transparent graphite layer, which was applied to the unexposed side of the film, completely changed the nature of the photodielectric response of the LDPE film (black square symbols in Figure 4). The presence of graphite on one side of the sample reduced the photo-induced increase in dielectric permittivity of LDPE. A saturation in the growth of the dielectric permittivity was observed. Taking into account that the effect mentioned was observed on a thin film of the polymer, it can be assumed that the contact potential between the graphite and LDPE caused weaker dipole photo-induction and/or lower mobility of photo-induced dipoles in the coated LDPE.

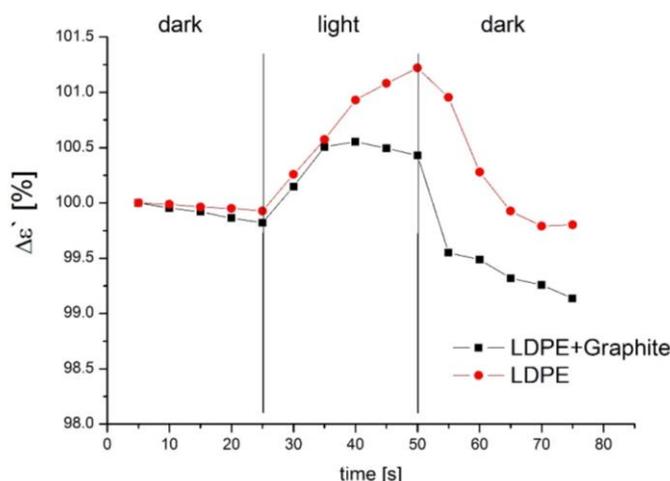


Figure 4. The relative changes in dielectric permittivity of thin film LDPE ($100 \mu\text{m}$) at $f = 10 \text{ kHz}$ due to illumination (white light, $P = 0.1 \text{ mW/m}^2$). Circle symbols (red) for LDPE and square symbols (black) for LDPE coated on one side with very thin (transparent) graphite layer

4. CONCLUSION

This paper presents the methodology for determining the dielectric parameters of film shaped materials in conditions of contactless dielectric measurements. The advantage of this method compared to the contact dielectric measurements is the ability to detect weakly expressed electrical phenomena in the material, which is illustrated by the example of the photodielectric response of LDPE. In addition, contactless dielectric measurements make it possible to determine the mobility of the charge carriers in the material in a simple way.

5. REFERENCES

[1] S. Günes, H. Neugebauer, N. S. Sariciftci, *Conjugated Polymer-Based Organic Solar Cells*,

Chem. Rev., Vol. 107 (2007) 1324–1338 (DOI: 10.1021/cr050149z).

[2] J. D. Myers, J. Xue, *Organic Semiconductors and their Applications in Photovoltaic Devices*, Polymer Reviews, Vol. 52–1 (2012) 1–37 (DOI: 10.1080/15583724.2011.644368).

[3] M. C. Barr, J. A. Rowehl, R. R. Lunt, J. Xu, A. Wang, C. M. Boyce, S. G. Im, V. Bulović, K. K. Gleason, *Direct monolithic integration of organic photovoltaic circuits on unmodified paper*, Adv. Mater, Vol. 23 (2011) 3500–3505 (DOI: 10.1002/adma.201101263).

[4] W. Hosakun, Y. Hosakun, D. Dudić, V. Djoković, L. Csóka, *Dependence of mechanical and electrical properties of silver nanocubes impregnated bacterial cellulose-silk fibroin-polyvinyl alcohol films on light exposure*, Polymer Testing, Vol. 71 (2018) 110–114 (DOI: 10.1016/j.polymertesting.2018.08.031)

- [5] T. M. Pavlović, D. D. Milosavljević, D. Mirjanić, L. S. Pantić, I. S. Radonjić, D. Pirsl, *Assessments and perspectives of PV solar power engineering in the Republic of Srpska (Bosnia and Herzegovina)*, Renewable and Sustainable Energy Reviews, Vol. 18 (2013) 119–133 (DOI: 10.1016/j.rser.2012.10.007).
- [6] N. A. Davidenko, S. V. Dekhtyarenko, A. V. Kozinets, A. S. Lobach, E. V. Mokrinskaya, V. A. Skryshevsky, N. G. Spitsyna, S. L. Studzinsky, O. V. Tretyak, L. S. Tonkopieva, *Photoconductive and Photodielectric Properties of Heterostructures Composed of PolyNEpoxypropylcarbazole and MEHPPV Films with a Zinc Octabutylphthalocyanine Additive*, Technical Physics, Vol. 56 (2011) 259–263 (DOI: 10.1134/S1063784211020101).
- [7] A. C. Arango, S. A. Carter, P. J. Brock, *Charge transfer in photovoltaics consisting of interpenetrating networks of conjugated polymer and TiO₂ nanoparticles*, Appl. Phys. Lett., Vol. 74 (1999) 1698 (DOI: 10.1063/1.123659).
- [8] L. Csóka, D. Dudić, I. Petronijević, C. Rozsa, K. Halasz, V. Djoković, *Photo-induced changes and contact relaxation of the surface AC conductivity of the paper prepared from poly(ethyleneimine)-TiO₂-anthocyanin modified cellulose fibers*, Cellulose, Vol. 22 (2015) 779–788 (DOI 10.1007/s10570-014-0537-3).
- [9] G. Chen, T. Y. G. Tay, A. E. Davies, Y. Tanaka, T. Takada, *Electrodes and charge injection in LDPE using the pulsed electroacoustic technique*, IEEE Transaction on Dielectrics and Electrical insulation, Vol. 8 (2001) 867–873 (DOI: 10.1109/94.971439).
- [10] R. P. Djajic-Jovanovic, D. L.J. Mirjanic, B. Nikin, J. P. Setrajcic and B. S. Tosic, *Stimulated absorption in ferroelectrics*, Journal of Physics C: Solid State Physics, Vol. 20 (1987) 5585–5600 (DOI:10.1088/0022-3719/20/33/016).
- [11] A. S. Luyt, E. H. G. Langner, D. Dudić, *Dielectric sensitization of zeolitic imidazolate framework-8 (ZIF-8) nanopowder*, Contemporary Materials, Vol. VIII-2 (2017) 180–183 (DOI: 10.7251/COMEN1702180L).
- [12] M. Edge, R. Janesa, J. Robinson, N. Allen, F. Thompson, J. Warman, *Microwave photodielectric and photoconductivity studies on titanium dioxide exposed to continuous, polychromatic irradiation; Part I: A novel analytical tool to assess the photoactivity of titanium dioxide*, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 113 (1998) 171–180 (DOI: 10.1010.6030/98/519.0).
- [13] A. S. Luyt, B. Škipina, L. Csóka, D. Dudić, *Charge-trapping capability and AC conductivity at different humidities of poly(ethyleneimine)-TiO₂-anthocyanin modified cellulose fibres*, Wood Sci. Tech., Vol. 52 (2018) 637–651 (<https://doi.org/10.1007/s00226-018-0994-1>).



БЕСКОНТАКТНА ДИЕЛЕКТРИЧНА МЕРЕЊА НА ПОЛИМЕРНИМ ФИЛМОВИМА

Сажетак: Диелектрична карактеризација материјала у РФ домену обично се изводи на узорцима са нанесеним електропроводним електродама. Висококвалитетан контакт између узорка и мерних електрода обезбеђује стабилан проток струје кроз узорак и информације о тачној вредности електричног поља у којем се налази узорак. Такође, омогућава да мерни инструмент на једноставан начин одреди диелектричне параметре испитиваног материјала. Међутим, присуство контактних потенцијала и размена наелектрисања између испитиваног материјала и примењених електрода могу маскирати неке електричне појаве у материјалу или значајно утицати на то како их опажамо. Да би се детектовали слабо изражени електрични процеси у материјалу, на пример фотоелектрични одзив неполарних полимера, потребно је извршити бесконтактна диелектрична мерења. Литература о бесконтактним диелектричним мерењима у РФ домену је сиромашна, и због тога је у овом чланку представљена методологија за одређивање диелектричних параметара материјала облика филма у условима бесконтактних диелектричних мерења.

Кључне речи: диелектрична мерења, бесконтактно, полимер, мобилност наелектрисања.

