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. doi:10.15199/48.2021.12.49

Research on dielectric parameters of epoxy resin based nanocomposites using the impedance spectroscopy method

Abstract. *Due to the modern requirements regarding the reliability of electrical devices operation, research on improving the parameters of materials and insulation systems, in particular high-voltage ones, used in the production, transmission and distribution of electricity is still valid. One of the research directions is the development and application of insulating materials modified with nanofillers. The paper presents the results of stability studies of selected dielectric properties of samples of insulation materials based on epoxy resin modified with titanium dioxide TiO_2 nanopowders. Changes in parameters caused by different wt% nanofiller content and their long-term stability after 10,000 hours from manufacturing are compared and analyzed.*

Streszczenie. *Współczesne wymagania dotyczące niezawodności pracy urządzeń elektrycznych powodują, że wciąż aktualnymi są badania dotyczące poprawy parametrów materiałów i układów izolacyjnych, w szczególności wysokonapięciowych, stosowanych w wytwarzaniu, przesyle i rozdziale energii elektrycznej. Jednym z kierunków badań jest opracowanie i zastosowanie materiałów izolacyjnych modyfikowanych nanowypełniaczami. Referat przedstawia wyniki badań stabilności wybranych właściwości dielektrycznych próbek materiałów izolacyjnych na bazie żywicy epoksydowej modyfikowanej nanoproszkami tlenku tytanu TiO_2. Porównane są i analizowane zmiany parametrów powodowane różną zawartością wt% nanowypełniacza oraz ich stabilność długoczasowa po 10.000 godzin od wytworzenia.* ***(Badania parametrów dielektrycznych nanokompozytów na bazie żywicy epoksydowej przy zastosowaniu metody spektroskopii impedancyjnej).***

Keywords: epoxy resin, titanium dioxide, nanocomposites, nanoparticles, nanodielectrics
Słowa kluczowe: żywica epoksydowa, dwutlenek tytanu, nanokompozyty, nanodomieszki, nanodielektryki

Introduction

The widespread use of electricity and modern requirements for the reliability of its supply to industrial, municipal and individual customers make it necessary to constantly improve the insulating systems of electrical devices. One of the most interesting solutions in this area of development are nanodielectrics, which have properties that often differ significantly from both components, basic polymers and nanoparticles from which they are made. Many research on nanodielectrics has shown that it is possible to obtain changes in the properties of dielectric materials in terms of modification of their different parameters [1]: volume resistivity, relative permittivity ε_r (dielectric constant), dielectric loss factor, electric strength, partial discharge resistance, thermal conductivity and resistance to thermal stresses, flame retardancy.

This new class of insulating materials can be used in the future as an advanced engineering material for instrument transformers, polymeric line and post insulators, bushings, power cables, rotating machines, etc. [2]. The possibility of a controlled change of material parameters values can be used, for example, to control the electric field distribution, both in AC and DC applications, or to optimize heat transfer processes in the insulation system.

It is obvious that the base material is a very important component of nanodielectrics. One of the most popular bases for creating nanocomposites is epoxy resin. Due to its advantages, it is widely used in the production of many electrical devices. It is characterized by good mechanical and electrical strength, very good adhesion to various substrates, low cost and low weight. Additionally, depending on the needs, it can take any shape [2].

Analyzing the literature sources, it can be noticed that a significant improvement in the dielectric properties of nanodielectrics is demonstrated by the use of such metal-oxide nanoparticles as: ZnO, MgO, TiO_2, SiO_2, $BaTiO_3$, Al_2O_3. The obtained test results sometimes differ from each other, which may be caused by differences in the methodology of sample production, heterogeneous dispersion of nanoparticles in the base material or different components of the nanocomposites formed [3, 4]. Nanoparticles are extremely small-size fillers with individual particle size in the 1 nm to 100 nm range [5]. The application of nanoparticles to the structure of the base creates an interfacial area in the material. Interphase occurs between a nanoparticle and a base polymer matrix. It is assumed that the area between the nanoparticle and the polymer matrix is the interaction zone with a radial dimension. The thickness of this area depends on the concentration of the nanofiller and the matrix used. The resulting interphase is basically a new material with properties different from those of the components from which the nanocomposite is created. The addition of even a small amount of nanofiller makes the interphase zone dominant [1, 6].

Due to the specificity of chemical reactions leading to cross-linking of the epoxy resin structure, this process is not completed during the production of the insulation system. This effect also applies to systems made of dielectric materials modified with nanofillers. For this reason, an interesting question is the long-term stability of the parameters of the nano-modified structure. The paper presents the results of research on the stability of the dielectric constant and the dielectric loss factor of samples of insulating materials produced on the basis of epoxy resin modified with titanium dioxide TiO_2 nanopowder. The values of these parameters, caused by different wt% nanofiller content (for large values of wt%, ranging from 5% to 15%), were measured and analyzed, and their long-term stability was also tested after 10,000 hours from manufacturing.

Sample preparation methodology

There is no doubt that the methodology of creating samples has a huge impact on the subsequent properties of the obtained nanocomposites. The choice of ingredients used is also very important. Currently, epoxy resins are often chosen as the base materials. The most commonly used composition for making nanocomposites is a mixture of epoxy resin (e.g. cycloaliphatic), hardener (usually anhydride) and nanofiller. The mixture may also contain an accelerator and a flexibiliser [7].

For the purposes of described research, groups of samples with dimensions of 100 mm x 100 mm x 1 mm were made. The samples were prepared on the basis of

Epoxylite 235SG resin, suitable for use at Class H temperatures. The nanofiller used was nanometric titanium dioxide TiO_2 powder with spherical shapes. The summary of all the sample groups is presented in Table 1. Each sample group contained 3 samples of the same type.

Table 1. Summary of the tested nanofilled epoxy samples

Sample group name	Sample composition	Sample dimensions [mm] length x width x thickness
05	Pure Epoxylite 235SG resin	100 x 100 x 1
06	Epoxylite 235SG resin + 5 wt.% TiO_2	100 x 100 x 1
07	Epoxylite 235SG resin + 10 wt.% TiO_2	100 x 100x 1
08	Epoxylite 235SG resin + 15 wt.% TiO_2	100 x 100 x 1

The methodology of producing nanocomposite samples may differ due to the type of epoxy resin used, the intended use of the sample, dimensions and shape of the sample, etc. There are many factors that may affect the sample formation process. Various methods of nanocomposite samples making can be found in the literature. Practices encountered when creating nanocomposite samples are also [7–13, 15, 18]:

- heating the mixture while blending;
- blending of reagents in a vacuum to reduce gaseous inclusions;
- drying the remaining reagents to remove moisture;
- gradual addition of reagents to obtain a uniform dispersion of processed nanoparticles in the mixture;
- post-curing of fabricated samples in a heating chamber at a specific temperature.

The samples prepared for presented research were made according to the following procedure [7–18]:

- drying the TiO_2 filler in the heating chamber to remove water, which can have a very negative effect on the nanocomposite (2h, 160°C);
- measuring the appropriate amount of reagents (epoxy resin, TiO_2 nanofiller, hardener), the percentage of each component in the final sample material was determined by weight;
- blending of reagents with a mechanical mixer. The time and intensity of blending depended on the consistency of the mixture. Due to the very short setting time of Epoxylite 235SG, all components except the hardener were mixed first. Then, after adding the hardener, blending was continued for about 3 minutes.;
- degassing the resin to remove gaseous inclusions (degassing was performed in a vacuum chamber with controlled pressure, 50 hPa);
- pouring the mixture into the molds (the pouring was performed under vacuum conditions);
- sample curing in a vacuum chamber with pressure ca. 500 hPa (the curing time depend on the type of epoxy resin);
- removing the solidified samples from the molds;
- storage of finished samples in a controlled and dry environment, without sunlight.

In the case of Epoxylite 235SG resin, the binding time for the mixture is about 30 minutes. This is an important parameter to consider when selecting an epoxy resin. Fast binding significantly reduces the time available for proper mixing all the reagents with the hardener. It may also limit the possibility of an acceptable degassing of the sample material. The consistency of the resulting composition is very important. Adding too much nanofiller makes the mixture more dense and difficult to process, it is also much harder to transfer it into the mold.

Experiment description

One of the research methods for testing parameters of insulating materials is the use of impedance spectroscopy IS [19]. This method allows to obtain a range of detailed information about the tested material. The most important parameters that can be acquired are the dielectric constant ε_r and the dielectric loss factor tgδ. Impedance spectroscopy measurements can be performed over a wide frequency range.

The measuring stand was equipped with a supervising computer, a Solartron 1260A frequency response analyzer (FRA) with a Solartron 1296A dielectric interface, and a dedicated sample holder (adjustable guard-ring air capacitor with a dial micrometer for precise determination of the sample thickness, placed in screened box). The samples were tested twice, about 200 hours after production and 10,000 hours later. The measurement was performed at AC low voltage signal (2 V) in the wide frequency range from 10^{-2} Hz to 10^4 Hz (series A - first measurements; new samples) and from 10^{-2} Hz to 10^5 Hz (series B - second measurements; stability verification).

Due to the low voltage stimulus, it can be assumed that the tested material is electrically linear; samples assumed to be LTI (linear time-invariant) object. The system's response to an applied AC voltage is the AC current, so it is possible to determine the real and the imaginary parts of the sample impedance. Due to the design of the measuring circuit and the electrode system, the inductance of the circuit may be omitted from the equivalent circuit in the frequency range used.

With the above data and known geometrical dimensions of the tested sample, the relative permittivity ε_r and the dielectric loss factor tgδ can be calculated. The analysis of dielectric parameters is based on the concept of complex capacitance (C' - real part, C"- imaginary part) or complex permittivity (ε' - real part, ε"- imaginary part). The dielectric loss factor tgδ is therefore determined as the ratio of the imaginary part to the real part [19, 20]:

$$\text{tg}\delta = C''/C' = \varepsilon''/\varepsilon' \tag{1}$$

Results and discussion

Figures 1 and 2 show the results of the measurement of the dielectric constant ε_r for A and B series of measurements. The graphs present the average values of ε_r calculated for the same type samples.

Based on Figures 1 and 2, it can be concluded that the increase in wt% the nanopowder admixture used increases the value of the dielectric constant of the obtained material. This means that the addition of TiO_2 nanofiller increases the capacitance of the sample made of nanomaterial. This effect can be used to control electric field distribution in layered or mixed insulation systems.

Value of ε_r decreases with increasing frequency. In the case of higher frequencies, rapid changes in the electric field stimulate the mechanism of electron and ion polarization. At the same frequencies the interfacial or dipole polarization may not be involved, as it is characterized by much greater inertia. Certain additives such as antioxidant and stabilizer may have been added during production. This, in turn, can translate into the formation of polar groups in the resin.

Comparing Figures 1 and 2, it can be stated that the storage of the samples under room conditions for 10,000 hours did not cause significant changes in the permittivity of the tested samples. Figures 3 and 4 show the measurement results of the dielectric loss factor tgδ. Figure 3 shows the results of measurements done 200 hours after samples production, while Figure 4 shows the results of the measurements done 10,000 hours later. Similarly to the measurement data for the relative permittivity ε_r, the presented graphs are the average values of all measurements done for the same type samples. Based on Figures 3 and 4, it can be concluded that the addition of titanium dioxide causes an increase in the value of the dielectric loss factor tgδ for all tested cases.

In order to analyze the long-term stability of the relative permittivity ε_r and the dielectric loss factor tgδ for individual groups of nanomaterials, the results obtained for them before and after 10,000 hours were compared (Figure 5 to Figure 8). After a long period of the samples conditioning, the continuous process of cross-linking the epoxy resin structure caused a slight increase in the dielectric constant value of the 05 series samples (unfilled resin, Figure 5), in the full range of the analyzed frequencies. In contrast, for the samples from series 08 (resin with 15 wt.% TiO_2, Figure 6), there was a slight decrease in the dielectric constant value, but the percentage change was smaller than for series 05.

Structural changes in the material of the samples, over the period of 10,000 hours of conditioning, caused a little decrease in the value of the dielectric loss factor tgδ in the lower frequency range for all tested samples (series 05 to 08). This effect is presented for the characteristics tgδ(*f*) of the 05 and 08 sample series (Figure 7 and Figure 8, resp.). Data analysis reveals that after the sample conditioning period, the range of the lowest dielectric loss values shifts to the left, towards lower frequencies. At the same time, the lowest value of the dielectric loss factor for each series of tested samples is noticeably reduced. This effect is shown for sample series 05 (unfilled resin, Figure 7) and sample series 08 (resin with 15 wt.% TiO_2, Figure 8).

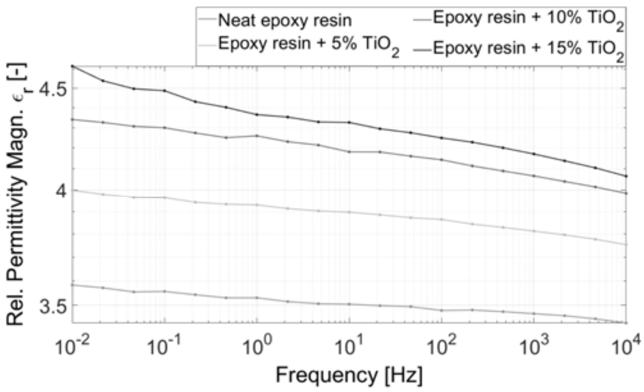

Fig.1. Dielectric constant ε_r vs. frequency - A series.

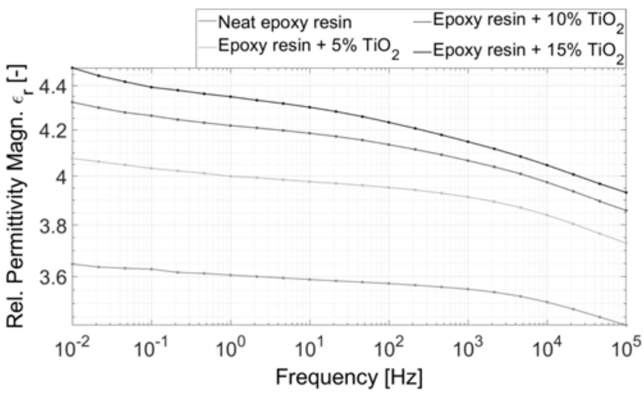

Fig.2. Dielectric constant ε_r vs. frequency - B series.

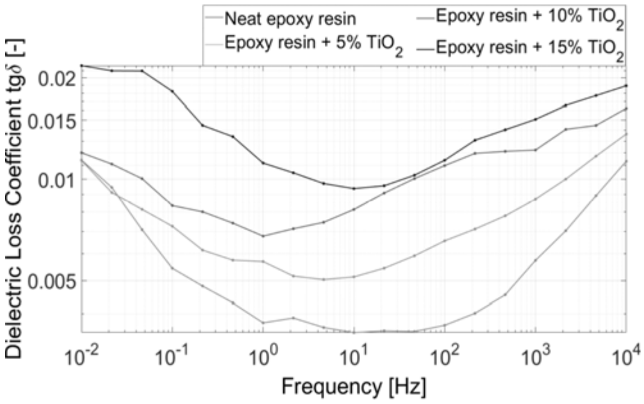

Fig.3. Dielectric loss factor tgδ vs. frequency - A series

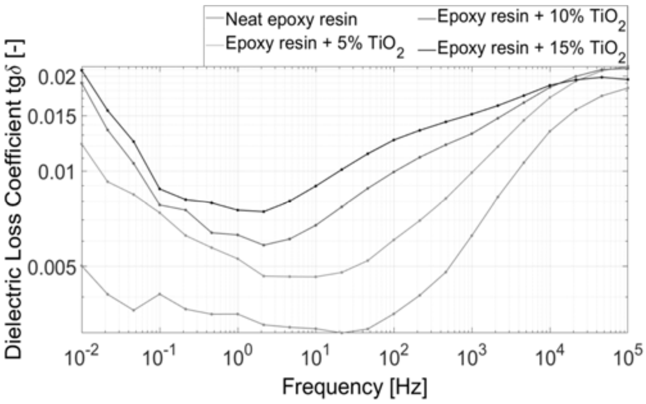

Fig.4. Dielectric loss factor tgδ vs. frequency - B series.

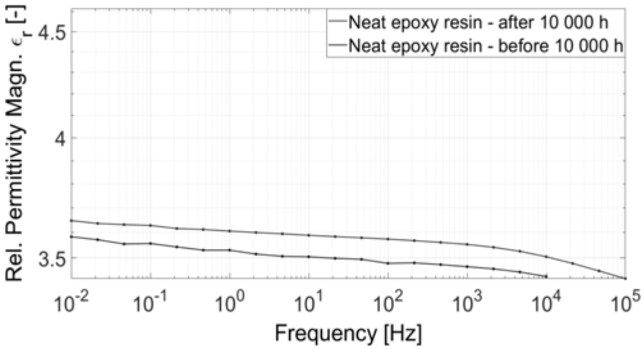

Fig.5. Dielectric constant ε_r vs. frequency – neat epoxy resin – comparison of measurement series A and B

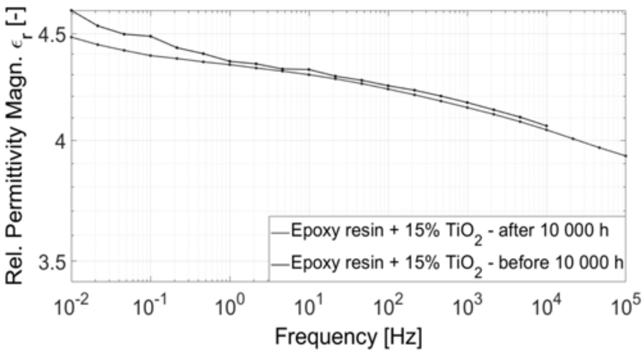

Fig.6. Dielectric constant ε_r vs. frequency – epoxy resin + 15%TiO_2 - comparison of measurement series A and B

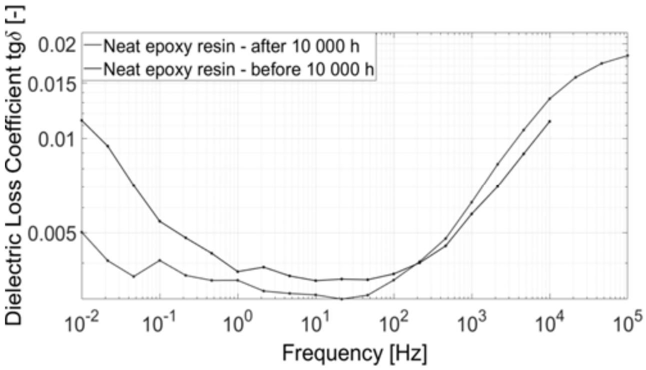

Fig.7. Dielectric loss factor tgδ vs. frequency – neat epoxy resin – comparison of measurement series A and B

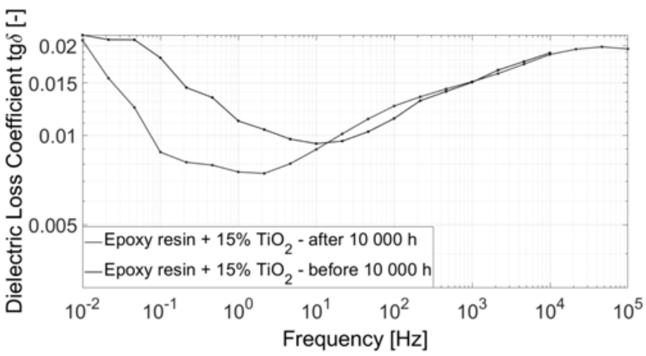

Fig.8. Dielectric loss factor tgδ vs. frequency – epoxy resin + 15%TiO_2 - comparison of measurement series A and B

Conclusions

The paper presents the results of measurements of the relative electric permittivity ε_r and the dielectric loss factor tgδ of samples made of epoxy resin filled with high wt% content of titanium dioxide TiO_2 nanopowder. The results of the laboratory measurements show that the addition of TiO_2 nanoparticles significantly changes the electrical properties of the tested samples compared to pure epoxy resin.

Additionally, the paper presents the results of a long-term stability study of the dielectric parameters of the sample material. The fabricated samples were stored for 10,000 hours under normal room conditions. Comparing the values of ε_r and tgδ before and after this time interval, it can be seen that the results of ε_r are very similar, while the values of tgδ mostly decrease in the lower frequency range.

The short cross-linking time of Epoxylite 235SG significantly limited the possibility of thorough mixing of all components. The use of a mechanical stirrer resulted in the appearance of a fairly large amount of gaseous inclusions in the mixture being processed. The required removal of these inclusions takes a long time, which makes it necessary to shorten the time of pouring the mixture into the molds to the necessary minimum, before the resin hardens. These factors can also result in the formation of significant local agglomerations of nanofillers. Agglomerations and strong interactions between the fillers and resin phases contribute to the increased importance of Maxwell-Wagner interfacial polarization [21].

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