

Article

Control of Dielectric Parameters of Micro- and Nanomodified Epoxy Resin Using Electrophoresis

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Abstract: This work presents the results of research on submicro- and nanocomposites with gradient properties, produced in a planned electrophoretic process. Epoxy-resin-based samples were filled with TiO₂ particles of three different sizes (13 nm, 38 nm, and <1 μm) at four different values of average electric field E_{av} (0.0 Vmm⁻¹, 125 Vmm⁻¹, 250 Vmm⁻¹, and 500 Vmm⁻¹) for 1 h each. Changes in selected dielectric parameters (dielectric constant ϵ_r and dielectric loss factor tan δ) of the composites were analyzed using broadband dielectric spectroscopy (10⁻¹ Hz to 10⁵ Hz). The influence of the E_{av} and the current $i(t)$ flowing through the sample material and the Joule heat generated in it on the resin curing process and the final gradient of dielectric parameters were investigated. The results show that the degree of modification of the ϵ_r gradient increases with increasing E_{av} and is more pronounced in the case of TiO₂ nanoparticles. The largest modifications in the ϵ_r and tan δ were obtained for nanoparticles with a diameter of 13 nm at E_{av} = 500 Vmm⁻¹, while the lowest for particles < 1 μm at E_{av} = 125 Vmm⁻¹. The effect of electrophoresis on the dielectric parameters is significant, especially near the anode region. Increasing the concentration of TiO₂ particles at the anode occurs at the expense of reducing their concentration in the remaining volume of the sample. The test results clearly demonstrate the importance of particle dimension and electric field strength for the gradient modification of the properties of the epoxy composite using electrophoresis. Numerical simulations of electric field stresses in the epoxy resin during the electrophoresis process, performed in the COMSOL program, revealed a significant increase in the E field strength in the areas close to the anode and cathode.

Keywords: electrophoresis; nanodielectrics; nanocomposites; functionally graded materials; epoxy resin; TiO₂; dielectric constant; dielectric loss factor; BDS; numerical simulation; COMSOL



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1. Introduction

The application of nanomaterial engineering technology to develop new electrical insulating materials and modify the functional properties of materials already used in the electric power industry is a response to the ever-increasing technical requirements set by producers and users of electrical devices [1–8]. These requirements result primarily from the constantly increasing rated power and voltage of power equipment, as well as from the need to achieve an appropriately high level of operational reliability of the devices. One of the ways to meet them is to increase the resistance of dielectric materials to complex operational stresses (electric, thermal, mechanical, and environmental [9,10]) and multiaspect optimization of the design of insulating systems. As a result, the goal of this type of modification should be to extend the estimated and actual life of the insulation. Due to the great importance and constant relevance of this issue, it remains the leading direction of work carried out throughout the entire evolution of the power industry, from its beginnings to the present day.

Materials commonly used as components in the insulation systems of electrical devices are polymeric composites, known for their favorable properties and the ability to modify their parameters in manufacturing processes [11–17]. One form of polymeric composites is epoxy resins filled with appropriate proportions of micro- or nanosized inorganic particles. In comparison to neat polymers, well-designed polymer-based composites significantly enhance the properties of insulation systems, encompassing electrical, thermal, and mechanical parameters. Such composites find applications in various areas of electrical insulation, including electronics, power electronics, microelectronics, energy storage technologies, and electrical engineering, especially in high-voltage applications [15–23]. They enable a reasonable compromise in material properties, enhancing certain aspects without markedly deteriorating others suitable for specific applications [4,14,24]. In this research area, the promising and effective strategy involves doping the polymer base with nanosized particles. Numerous studies unequivocally indicate that the properties of nanocomposites are much more favorable compared to unfilled polymers or those modified with microfillers. Even adding a small amount of nanometric inorganic materials to various polymer structures enables the creation of new materials with high potential across various applications. The modification of the properties of nanocomposites is related to the presence of a large interface, the volume fraction of which increases with the reduction in the size of the filler particles. The interface depends on the interaction between the base material and the nanofiller, leading to changes in material structure, alterations in polymer chain segment mobility, curing behavior, or crystallinity [1–4,25,26].

Functionally graded materials (FGMs) constitute a specific type of composite materials. The structure of most insulation systems is subjected to various anisotropic stresses during operation. For instance, this may include a nonuniform electric field concentrated around a highly curved electrode, affecting the stress distribution of the electric field E , or disparities in thermal expansion coefficients at the interface of different materials in a layered structure. The solution to such problems may lie in the application of materials with structures in which at least one parameter, such as resistance or dielectric constant, depends on the linear or spatial location (i.e., there is a gradient of the value of a specific parameter) [21,27–33]. The concept behind using FGMs is to ensure a smooth change in the value of the selected parameter between adjacent layers of material or elements of the system. This allows for the elimination or at least mitigation of issues associated with abrupt, discontinuous changes in properties in boundary areas. The gradual, controlled variation of parameters enables better adaptation of the insulation system design to anticipated operating conditions. Gradient materials find applications in nearly all fields of technology, including aerospace, space exploration, automotive, machinery, electronics, and medicine [34,35].

Various methods and technologies are employed for the production and modification of FGMs, including lamination technology [36,37], layer-by-layer casting technique [38], methods utilizing centrifugal force [39–41], 3D printing combined with vacuum casting [42], gravity separation [43], electrodeposition [44–47], dielectrophoresis [48], magnetron sputtering [49], magnetophoresis [50], or methods based on the use of polymer composites with nonlinear resistivity, depending on the value of the applied voltage (or the local electric field E) [27,28,51,52]. Each of the mentioned methods has its specific challenges and limitations. Lamination technology does not ensure a one-time integral forming, often leading to defects at the interface of different materials. In the spinning (centrifugal) method, due to the acting forces, the material gradient changes proportionally to the square of the distance from the axis of rotation (αr^2). The greater the distance from the axis of rotation (larger radius r), the greater the change in the gradient value of the parameter in the material. This excludes its application in insulation system designs requiring a different distribution. The electrodeposition method has various variants depending on the type of insulation system in which the FGM is produced. The magnetophoresis method exhibits a degree of flexibility; however, generating a strong magnetic field similar to the distribution of the electric field is challenging [53].

An effective method for producing gradient materials can be the electrophoresis method [21,30,31,46,47,53,54]. Electrophoresis is an electrokinetic phenomenon involving the movement of charged particles under the influence of an external electric field in a continuous medium, whether liquid or gel-like [55]. This results in charge and mass transport processes, altering the local particle concentration displaced in the base material (suspending medium) by electric forces. As shown in Figure 1, if the particle has a negative charge (anion), the electric field E forces it to move towards the anode (anaphoresis process), and if the particle's charge is positive (cation), the particle migrates towards the cathode (cataphoresis process).

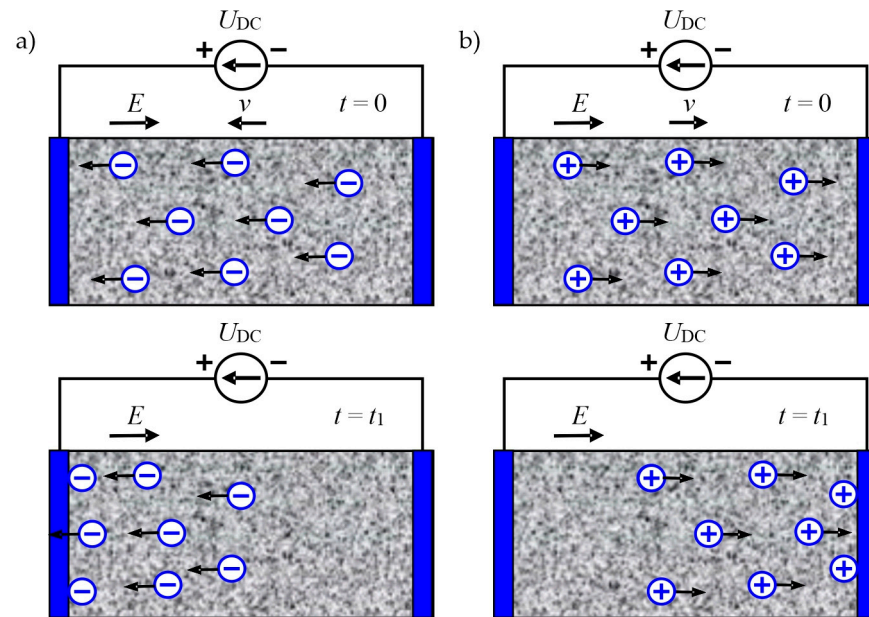


Figure 1. Illustration of the electrophoretic process of charged particles moving under the influence of the electric field E in the suspending medium: (a) anaphoretic (anodic) process; (b) cataphoretic (cathodic) process.

When a particle with a charge q is present in a DC electric field E , the electrophoretic force F_{ep} acting on the particle in the suspending medium is given by

$$F_{ep} = qE \quad (1)$$

A parameter describing the mobility of a charged particle in the suspending medium under the influence of the electric field E is its electrophoretic mobility μ_{ep} , defined as follows [55,56]:

$$\mu_{ep} = \frac{v}{E} \quad (2)$$

where

v —particle's velocity (for constant velocity it is the distance migrated by the particle divided by the migration time).

If the particle is spherical, and the electrophoretic force F_{ep} acting on it is equal to the frictional force F_f , considering Stokes' law, the electrophoretic mobility can be expressed using the following equation [55,57,58]:

$$\mu_{ep} = \frac{q}{6\pi\eta r} \quad (3)$$

where

q —effective electric charge of the particle;

η —dynamic viscosity of the medium in which the particle moves;

r —radius of the particle.

In the classic approach, developed for colloidal systems, the movement of the dispersed phase (charged particles), caused by the electric field E , in relation to the dispersion phase (suspending medium) is analyzed. The electrophoretic force then depends on the particle's charge, the electric field strength, the delay caused by the diffusive layer (according to the theory of the double electric layer), and the conductivity of the particle and the medium, as well as the size and shape of the particle [59–61]. When the thickness of the double layer is significantly smaller than the size of the particle, the universal equation for determining the mobility of particles of any size, shape, and orientation relative to the applied field E is the Smoluchowski equation [55,62]:

$$\mu_{ep} = \frac{\varepsilon_m \zeta}{\eta} \quad (4)$$

where

ε_m —permittivity of the suspending medium, $\varepsilon_m = \varepsilon_r \cdot \varepsilon_0$;
 ε_r —dielectric constant of the suspending medium;
 ε_0 —permittivity of the vacuum ($8.85 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$);
 ζ —zeta (electrokinetic) potential.

The double electric layer plays a crucial role in the analysis of the electrophoresis phenomenon, as interactions associated with it constitute one of the main physical mechanisms influencing the motion of particles. The theory of the double layer explains the interaction of electric charges distributed around a particle suspended in a solution. The first layer consists of ions adsorbed onto the particle's surface, forming a surface charge. This charge is balanced by ions of opposite sign. Some counter-ions may be directly associated with the particle's surface, while others will form a diffusive layer near the surface. In this layer, ions exhibit higher mobility. As the particle moves, the ions within the boundaries of the double electric layer move along with it, while outside the double layer, ions no longer move with the particle. The electric potential at this boundary is called the zeta potential ζ , i.e., the electrokinetic potential at the slipping plane of the double electric layer [53,55,62,63].

Electrophoresis is utilized across diverse scientific and technological domains. In manufacturing processes, electrophoretic deposition (EPD) is particularly favored for its capability to produce coatings on various materials. Among the key advantages of this method are the ability to form coatings on objects with complex 3D geometries, uniform distribution of the coating, effective coverage of surface defects (depressions, irregularities), applicability to different materials (ceramics, metals, polymers), and the high resistance of the resulting coatings to corrosion and mechanical wear, ensuring a longer lifespan for the processed product. The main drawback of the EPD method is the necessity for the use of specialized and costly processing equipment [64,65].

In a series of publications [21,30,31], an innovative application of electrophoresis was proposed and experimentally verified for producing a composite material with a dielectric constant gradient distribution. The aim of these studies was to control the E field distribution in power electronics applications. To achieve this effect, the volume concentration of SrTiO_2 ceramic particles, serving as the filler in the base thermosetting epoxy resin, was modified during the electrophoretic process. The obtained results confirmed the feasibility of manufacturing FGMs using the electrophoresis method. Simultaneously, the authors concluded that, for the purpose of controlled modification of the permittivity of the epoxy composite, it is also suggested to consider the use of other fillers with high ε_r , such as BaTiO_3 , TiO_2 , ZnO , or SiC .

In this article, the results of manufacturing and testing of FGM samples consisting of epoxy polymer filled with TiO_2 particles are presented. The electrophoresis process, used for permittivity modification, was conducted under controlled conditions. The dispersed phase included TiO_2 particles in three different sizes (13 nm, 38 nm, and $<1 \mu\text{m}$), while the dispersing phase was epoxy resin. An analysis was conducted to examine the influence

of filler particle size and applied electric field stress on the achieved gradient of dielectric constant in the composite material. The electrophoretic process in the sample material was observed by (1) recording the current $i(t)$ flowing through the sample during the application of a constant voltage, generating an electric field E and electrophoretic force F_{ep} , and (2) monitoring the surface temperature of the sample using a thermal camera during the voltage-controlled electrophoretic process. For the produced FGM samples, location-dependent, broadband characteristics of dielectric constant (relative permittivity) ϵ_r and the dielectric loss factor $\tan\delta$ were determined over a frequency range from 10^{-1} Hz to 10^5 Hz (6 decades). The research confirmed the possibility of using TiO_2 fillers to produce AC insulating systems with spatial modification of permittivity through electrophoretic processes. This can be achieved even when the resin gelation time is relatively short (then the E field-stimulated movement of charged particles suspended in the resin is still possible) and with a large distance between the electrodes (20 mm).

2. Experiment Description

2.1. Materials for Tested Samples

In the conducted research, FGM samples were prepared using epoxy resin filled with titanium dioxide TiO_2 particles. The base polymer used was the epoxy resin Epoxylite[®] 235SG (Elantas, Hamburg, Germany), which is based on diglycidyl ether of bisphenol A (DGEBA) [66]. The curing agent used for the resin is an aliphatic amine-based hardener with a weight ratio of 5:1 (resin to hardener). Epoxy resins of this type are commonly applied in the electrical industry, and their properties are well established [67–73]. The gelation time of the applied resin at 25 °C is approximately 35 min (2100 s). The viscosity of the epoxy resin and hardener mixture at 25 °C is 1650 mPa·s, and the density of the cured neat resin is 1.13 g·cm^{−3}. The resin can withstand prolonged exposure to a temperature of 180 °C (Class H insulation), making it suitable for various electrical applications [66].

As a filler for the composite specimens, particles of TiO_2 with three different sizes were used: 13 nm and 38 nm (Nanografi Nano Technology, Ankara, Turkey) [74,75] and <1 µm (Acros Organics, Geel, Belgium) [76], i.e., representing two nanosized and one submicron-sized fillers. The TiO_2 nanoparticles used in the experiment are in the anatase form. This form of titania has a specific density of 3.894 g/cm³, and the value of its dielectric constant reported in the literature sources is 18.9 to 55 [77–80], i.e., it is much lower than in the rutile form. TiO_2 is the most durable and widely used of all titanium oxides. Its popularity in the industry is driven by high thermal and chemical stability, nontoxicity, optoelectronic properties, high photocatalytic properties, and acceptable cost [81–84].

2.2. Preparation and Processing of Samples

To prepare the composite samples, a multistage procedure was implemented based on published works by other research teams as well as on our own practical laboratory experiences [85–90]. In the initial stage, the filler powders were dried in a high-precision analytical balance Ma 50/1.R.WH (Radwag, Radom, Poland). The drying temperature for each filler was set at 160 °C. The drying process continued until a stable weight reading of the filler load was achieved, serving as an indicator of moisture removal from the micro/nanopowder.

In the second stage, a specified weight of the filler (TiO_2 particles) was added to the epoxy resin and mixed using a mechanical mixer. Each time, for the preparation of a composite sample, the base epoxy resin was blended with 10 wt% TiO_2 . Due to the density of the mixture, the mechanical mixing process lasted for 15 min. In the subsequent stage, the appropriate amount of curing agent was added to the resin–filler mixture, and mechanical mixing was continued for an additional 5 min. The delayed addition of the curing agent in the final mixing phase is due to the gelation time declared by the epoxy resin manufacturer. When preparing the samples, it was considered that a repeatable and correctly conducted mixing process ensures the creation of a composite with an even

dispersion of filler particles in the base polymer, thus allowing the production of samples suitable for comparative measurements and tests.

After mixing the components, the liquid composite mixture was placed in a vacuum chamber to eliminate gas bubbles (degassing at a pressure of 2.5 kPa for 5 min) [90]. The prepared resin with TiO_2 filler was then applied to the prepared molds. Each mold consisted of two flat stainless steel electrodes, with a length $l = 100$ mm and a separation distance $d = 20$ mm, attached to the flat bottom of the mold made of Teflon[®] (Figure 2). The corners of both electrodes were rounded to eliminate edge effects. The liquid composite was poured into the molds between the electrodes, and then, for 1 h, subjected to the action of an electric field E , generated after applying a DC voltage at a fixed value to the electrode system (Figure 3).

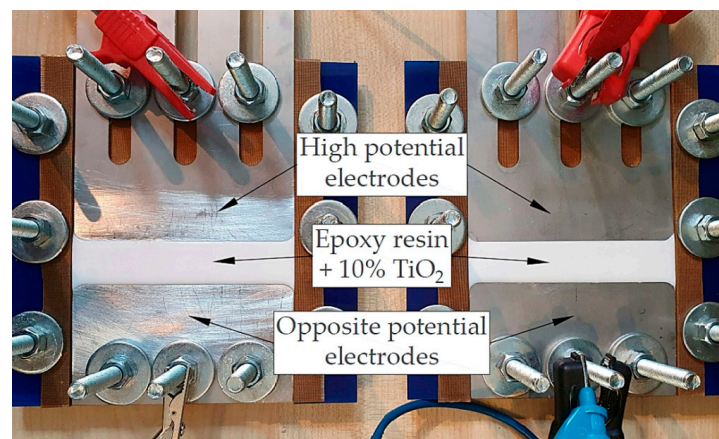


Figure 2. Molds for producing FGM samples using the electrophoresis method. The dimensions of the sample in the area between stainless steel electrodes are 100 mm × 20 mm × 2 mm.

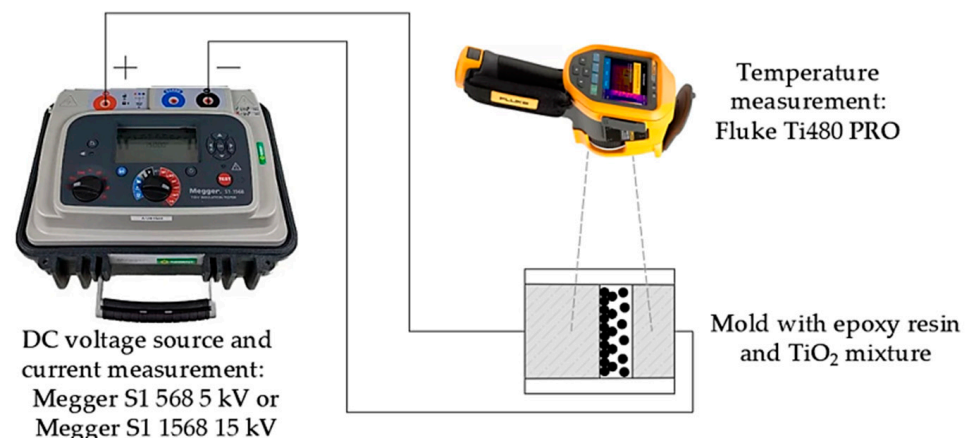


Figure 3. Laboratory setup for producing FGM samples using the electrophoresis method, including the recording of current and sample surface temperature.

For electrophoretically modified samples (12 groups of specimens), three different DC voltage values of U_{DC} were applied: 2.5 kV, 5.0 kV, and 10.0 kV, supplied by the insulation resistance tester Megger S1 568 (5 kV) or Megger S1 1568 (15 kV) (Megger, Dover, UK). Considering Equation (5), the average values of the electric field strength E_{av} between the electrodes were $125 \text{ V} \cdot \text{mm}^{-1}$, $250 \text{ V} \cdot \text{mm}^{-1}$, or $500 \text{ V} \cdot \text{mm}^{-1}$, respectively.

$$E_{av} = \frac{U_{DC}}{d} \quad (5)$$

The electrophoresis process can be stimulated by an external voltage or current source. In the case of a suspending medium (material sample) with constant resistivity in its volume, both systems ensure identical, constant process conditions. When the resistivity distribution of the suspension medium (sample material) changes during the electrophoresis process, the E field in the sample volume is not constant. If a constant current source is used, there is also a change in the E_{av} value, proportional to the change in sample resistance. When the increase in total resistance is significant, there may be an undesirably large increase in the voltage value on the forming electrodes (up to the supply voltage limit value).

To verify the influence of the electrophoresis process on the dielectric parameters of the composites, reference samples were also prepared in each group without the application of the electric field E . Both applied voltage sources allowed the recording of the current flowing through the composite material during the electrophoresis process. Simultaneously, the surface temperature of the sample was recorded using a Ti480 PRO (Fluke, Everett, WA, USA) thermal imaging camera (Figure 3) during each of these processes. After one hour, the voltage was turned off, and the sample was left for initial curing for 2 days. After this period, the sample was removed from the mold and further cured in a heating chamber at 130 °C for 8 h. The finished samples were cooled and stored in a dry, dark place at room temperature (21 °C to 23 °C). In each group of samples, at least two specimens with dimensions of 100 mm × 20 mm × 2 mm (± 0.1 mm) were prepared. Table 1 lists 16 groups of samples for which dielectric parameters were measured and compared.

Table 1. Overview of groups of tested samples (reference groups are marked in green).

Samples Set No.	Sample Composition	Applied Voltage U_{DC} , kV	Average Electric Field Strength E_{av} , V·mm ⁻¹
1	epoxy resin + 10 wt% TiO ₂ 13 nm	0.0	0.0
2	epoxy resin + 10 wt% TiO ₂ 13 nm	2.5	125
3	epoxy resin + 10 wt% TiO ₂ 13 nm	5.0	250
4	epoxy resin + 10 wt% TiO ₂ 13 nm	10.0	500
5	epoxy resin + 10 wt% TiO ₂ 38 nm	0.0	0.0
6	epoxy resin + 10 wt% TiO ₂ 38 nm	2.5	125
7	epoxy resin + 10 wt% TiO ₂ 38 nm	5.0	250
8	epoxy resin + 10 wt% TiO ₂ 38 nm	10.0	500
9	epoxy resin + 10 wt% TiO ₂ < 1 µm	0.0	0.0
10	epoxy resin + 10 wt% TiO ₂ < 1 µm	2.5	125
11	epoxy resin + 10 wt% TiO ₂ < 1 µm	5.0	250
12	epoxy resin + 10 wt% TiO ₂ < 1 µm	10.0	500
13	neat epoxy resin	0.0	0.0
14	neat epoxy resin	2.5	125
15	neat epoxy resin	5.0	250
16	neat epoxy resin	10.0	500

2.3. Measurement of Wideband Dielectric Properties of Composite Samples

To determine the dielectric properties of the obtained composite samples, the frequency domain spectroscopy (FDS) method was employed, allowing for the analysis of relative permittivity and dielectric loss factor based on impedance measurements conducted over a broadband frequency range [91]. Measurements were performed using the Solartron 1260A impedance/gain-phase analyzer [92] with the Solartron 1296A dielectric interface [93] (Solartron Analytical, Farnborough, Hampshire, UK). This setup serves as a high-precision frequency response analyzer, enabling the determination of the real and imaginary components of impedance and, considering the measured sample's geometry, the broadband dielectric parameters of the tested material. The recorded measurement data

were post-processed and analyzed using dedicated MATLAB® R2022b (MathWorks, Inc., Natick, MA, USA) software procedures. The measurement system consisted of a control computer, a Solartron 1260A analyzer, a Solartron 1296A dielectric interface, and a system of two parallel measurement electrodes, each with a diameter of 5 mm, made of stainless steel (Figure 4).

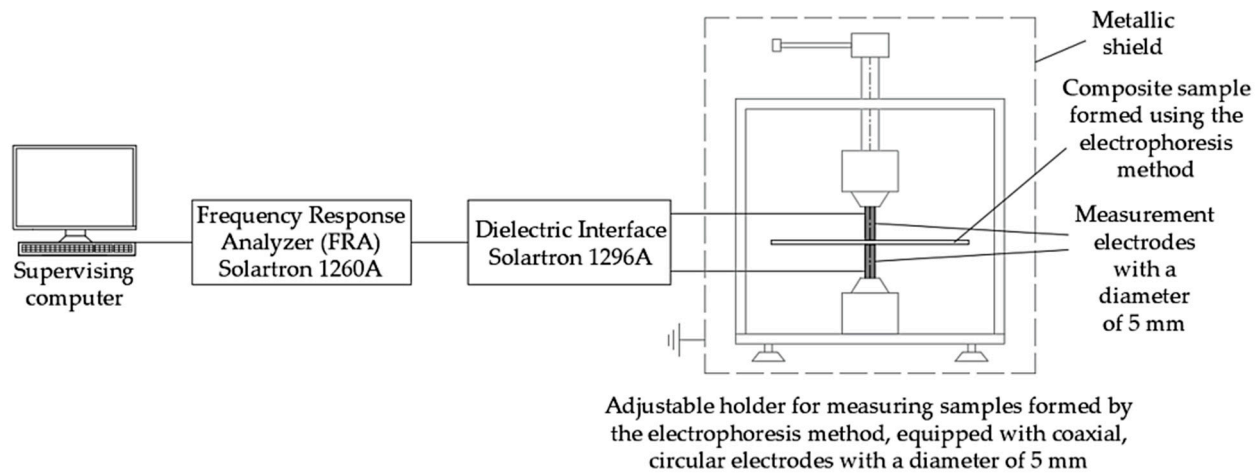


Figure 4. Measurement setup for determining dielectric properties of composite samples.

For each tested sample, measurements of the dielectric parameters of the composite material were conducted in 9 areas with the same geometric configuration (Figure 5). Measurement points 1, 4, and 7 are located near the edge of the sample adjacent to the electrode with a high potential (anode), while measurement points 3, 6, and 9 are near the edge of the sample adjacent to the electrode with a low potential (cathode). A micrometer with a resolution of 0.005 mm was used to precisely determine the thickness of the tested samples at the measurement locations. All measurements were performed at room temperature (approximately 23 °C), in the frequency range from 10^{-1} Hz to 10^5 Hz, at an AC voltage with an effective value of 3 V. Due to the very low level of recorded current signals, the measuring electrode system along with the tested sample of the composite material was placed in a Faraday cage to reduce the influence of external electromagnetic interference.

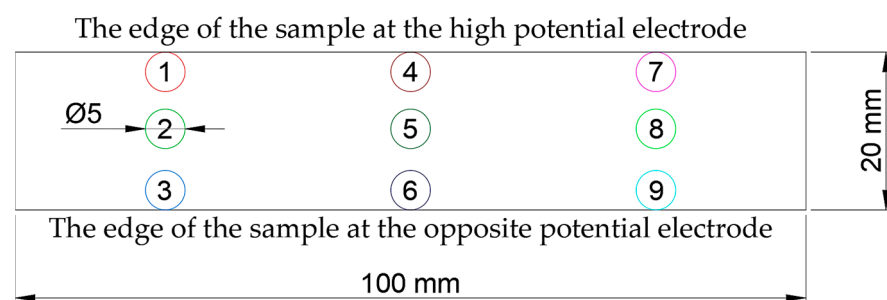


Figure 5. Geometric locations of areas of the composite sample for which broadband measurements of dielectric parameters were made.

3. Results of Processing and Measurement of Composite Samples

3.1. Observation of Samples Processed in a DC Electric Field

The one-hour electrophoretic process of forming composite samples, made from epoxy resin filled with 10 wt% TiO₂ particles of different sizes, was observed by

- Recording the current flowing through the sample during the application of the electric field E , inducing the electrophoretic movement of charged particles;
- Recording the temperature at the central point of the sample's surface and capturing thermal images of the entire sample surface.

Both insulation testers (Megger S1 568 and Megger S1 1568), used as DC voltage sources generating the E field in composite samples, allowed for the measurement and computer recording of the current flowing through the sample every 1 s (current sampling frequency $f_p = 1$ Hz). In Figure 6, recorded profiles of the current $i(t)$ and the temperature of the sample surface at its central point $\vartheta(t)$ are presented for samples without filler (neat epoxy resin) and for epoxy resin samples filled with TiO_2 particles of various sizes: 13 nm, 38 nm, or $< 1 \mu\text{m}$. In the presented example of current and temperature observations, the voltage applied to the electrodes was 10 kV in each case. Temperature changes were monitored for samples subjected to the influence of the E field as well as for control samples formed without the presence of an electric field ($U_{\text{DC}} = 0.0$ V). Figure 7 shows similar time profiles of current and temperature for neat resin and samples filled with TiO_2 particles $< 1 \mu\text{m}$ in size for different DC voltages applied to the electrodes: 2.5 kV, 5.0 kV, and 10.0 kV. The temperature values of the central point of the surface of each of the observed samples, used to plot the temperature curves $\vartheta(t)$, were taken from thermal images recorded by the camera every 1 min.

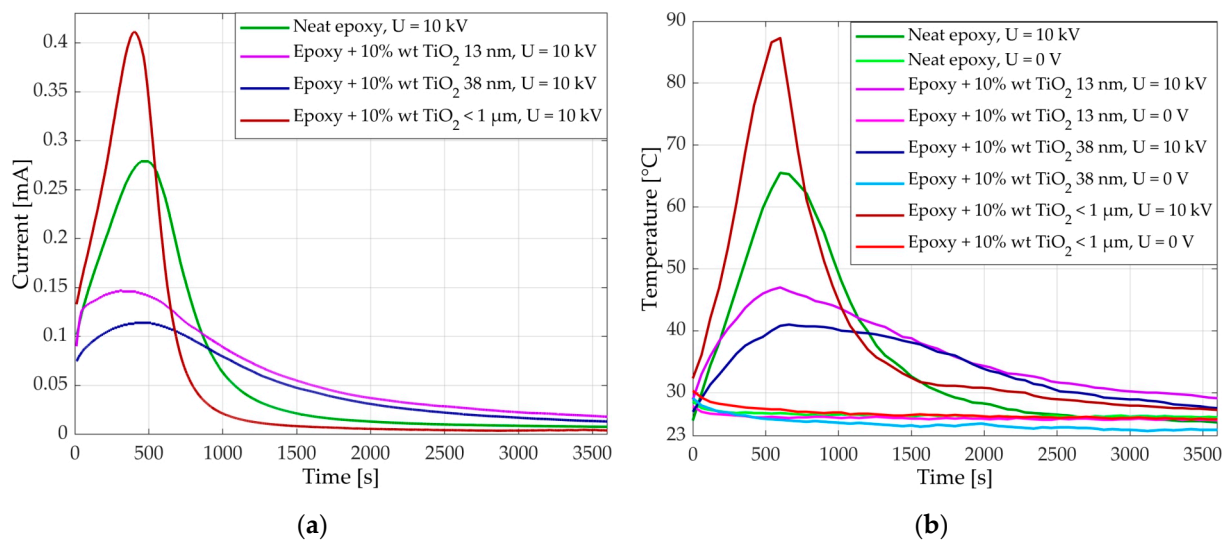


Figure 6. Registered time characteristics of the current $i(t)$ flowing through the sample during its stimulation by the E field, causing the occurrence of the electrophoresis process of TiO_2 particles (a), and the time characteristics of the temperature at the central point of the sample surface $\vartheta(t)$ during its electrophoretic formation (b), depending on the size of the filler particles. Voltage on the electrodes: 10 kV.

For each of the specimens subjected to a voltage of 10 kV (i.e., during the occurring electrophoresis process in the composite), thermal images of their surfaces were also recorded (Figures 8–11). Color-coded images depict the thermal state of samples filled with TiO_2 particles of average sizes 13 nm (Figure 8), 38 nm (Figure 9), $< 1 \mu\text{m}$ (Figure 10), and the neat, unfilled epoxy resin sample (Figure 11). Each of the figures presents four selected thermograms, recorded at 1, 10, 25, and 50 minutes from the start of the electrophoresis process (blue corresponds to the lowest temperature and red to the highest; note: temperature scales are different for individual images; the temperature of the central point for each thermal image is indicated).

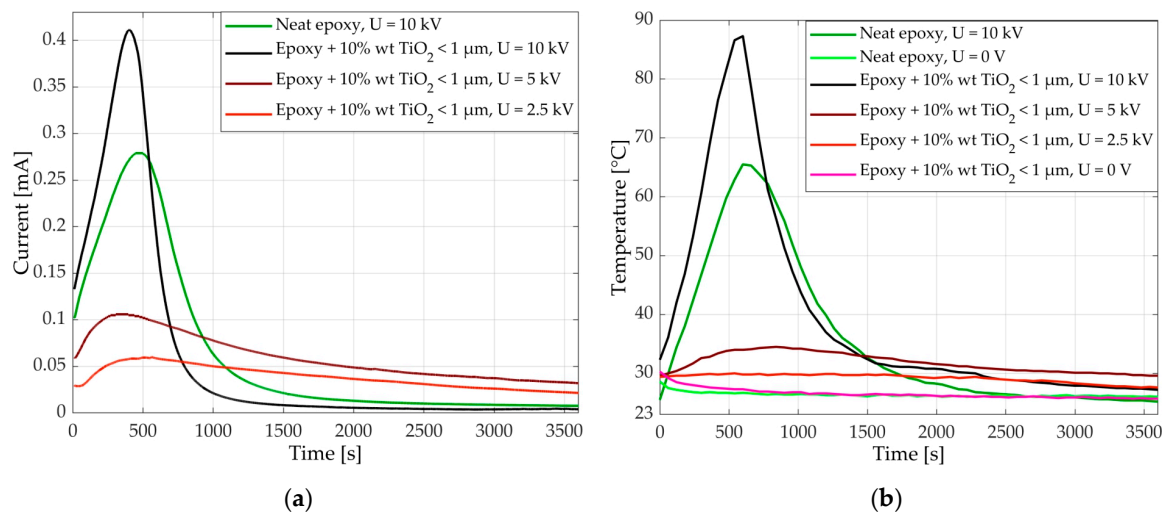


Figure 7. Registered time characteristics of the current $i(t)$ flowing through the sample during its stimulation by the E field, causing the occurrence of the electrophoresis process of TiO_2 particles (a), and the time characteristics of the temperature at the central point of the sample surface $\vartheta(t)$ during its electrophoretic formation (b), for filler particles with a size $< 1 \mu\text{m}$, depending on the voltage applied to the electrodes (0.0 kV, 2.5 kV, 5.0 kV, and 10.0 kV).

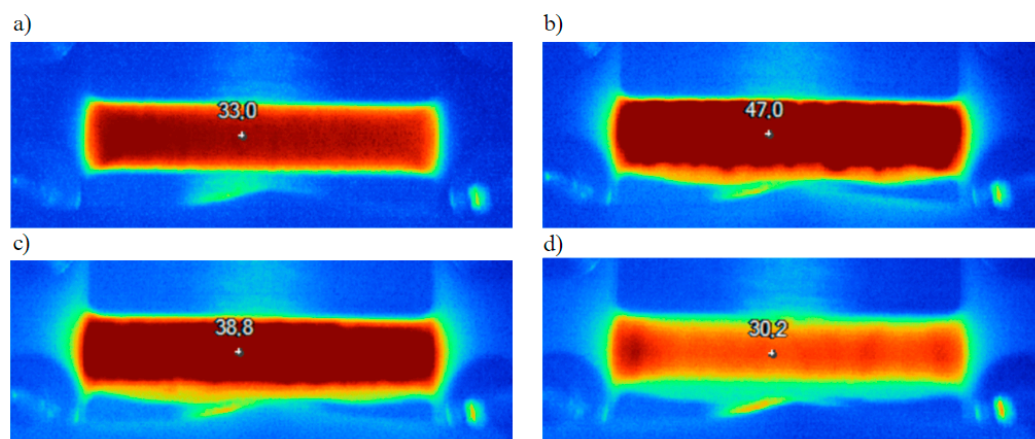


Figure 8. Thermal images of the surface of the composite sample filled with TiO_2 13 nm at a voltage of 10 kV, recorded after (a) 60 s, (b) 600 s, (c) 1500 s, and (d) 3000 s.

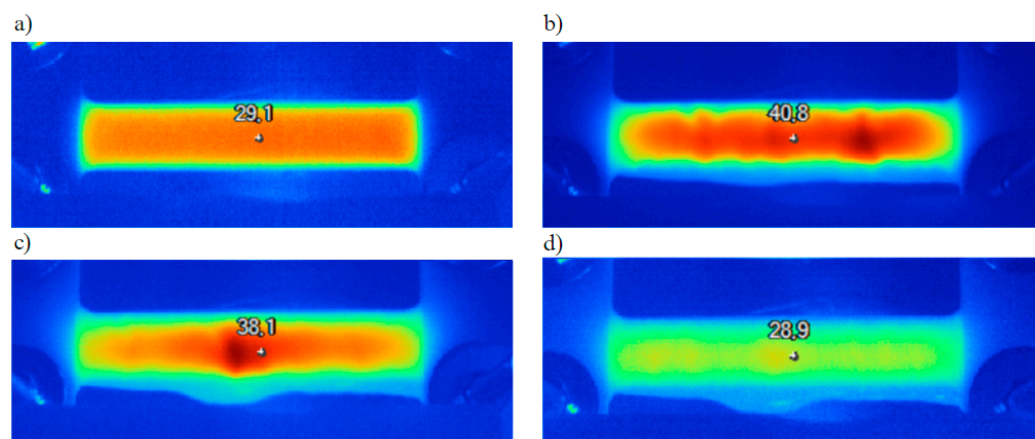


Figure 9. Thermal images of the surface of the composite sample filled with TiO_2 38 nm at a voltage of 10 kV, recorded after (a) 60 s, (b) 600 s, (c) 1500 s, and (d) 3000 s.

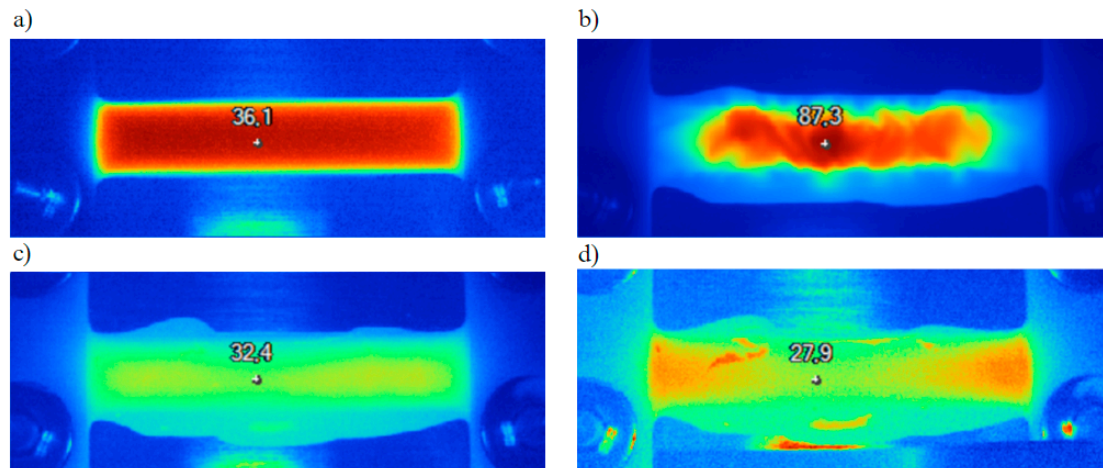


Figure 10. Thermal images of the surface of the composite sample filled with $\text{TiO}_2 < 1 \mu\text{m}$ at a voltage of 10 kV, recorded after (a) 60 s, (b) 600 s, (c) 1500 s, and (d) 3000 s.

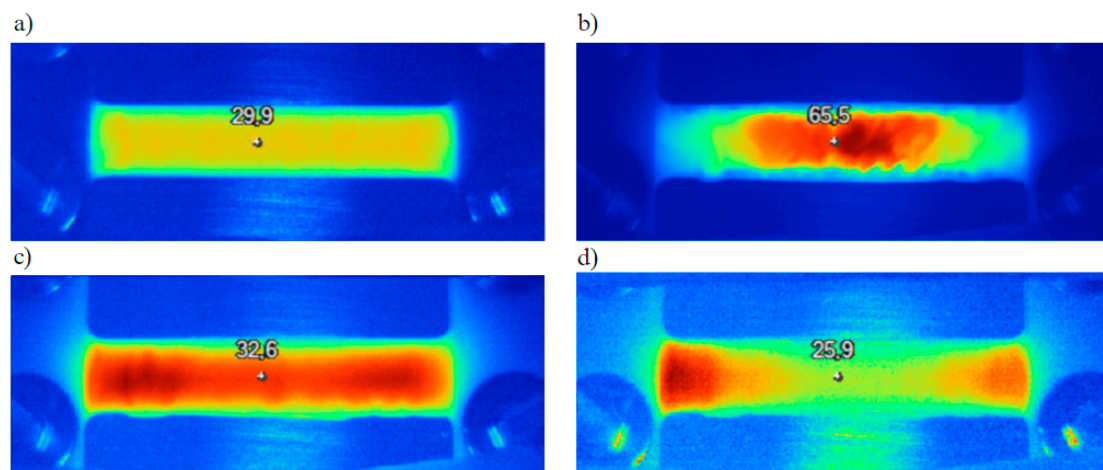


Figure 11. Thermal images of the surface of the neat epoxy resin sample at a voltage of 10 kV, recorded after (a) 60 s, (b) 600 s, (c) 1500 s, and (d) 3000 s.

3.2. Results of Broadband Measurements of Dielectric Parameters

Figures 12–17 show the results of broadband measurements of ϵ_r (Figures 12–14) and $\tan\delta$ (Figures 15–17) in nine selected areas (Figure 5), for each group of samples. Changes in the values of these parameters were analyzed and compared over a frequency range from 10^{-1} Hz to 10^5 Hz. Twelve sample groups produced in processes with modified parameters, as specified in Table 1 (three sizes of TiO_2 filler particles and four values of the electric field E_{av}), were investigated. Additionally, measurements of the mentioned parameters were also carried out for samples produced from neat epoxy resin without any filler (Figure 18). These results served as a reference for the discussion and assessment of the impact of fillers on the dielectric properties of composite samples.

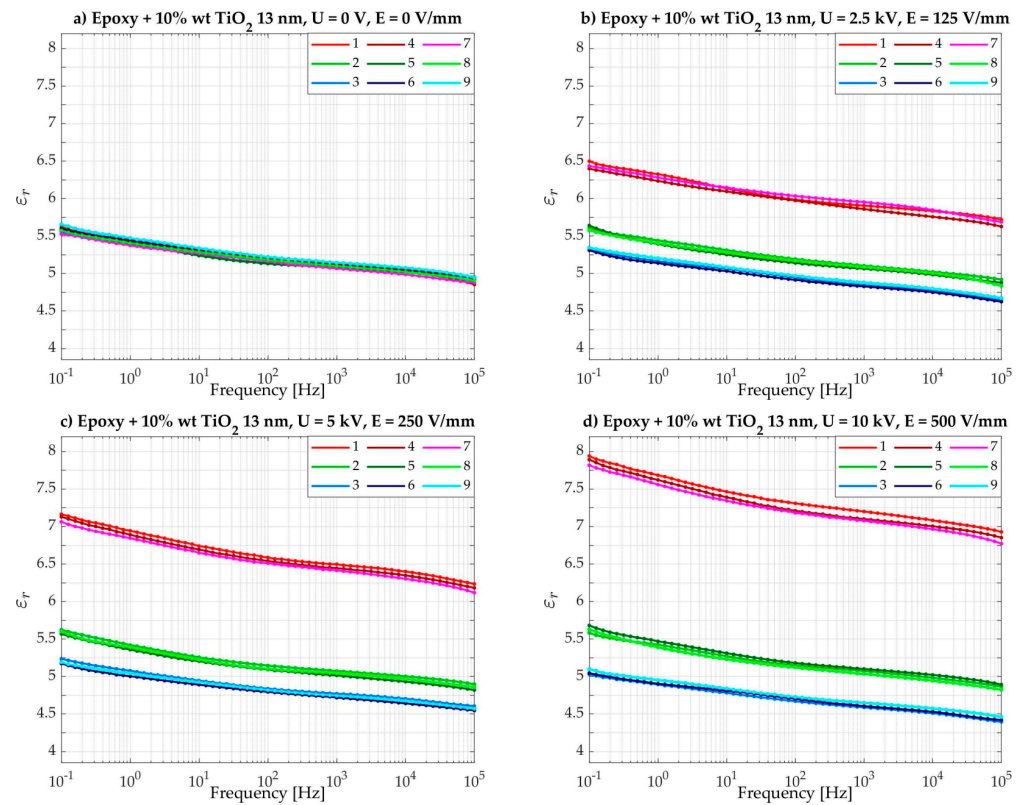


Figure 12. Broadband characteristics of ϵ_r for samples with TiO_2 13 nm filler. Applied electric field stress E_{av} : (a) $0.0 \text{ V}\cdot\text{mm}^{-1}$, (b) $125 \text{ V}\cdot\text{mm}^{-1}$, (c) $250 \text{ V}\cdot\text{mm}^{-1}$, and (d) $500 \text{ V}\cdot\text{mm}^{-1}$.

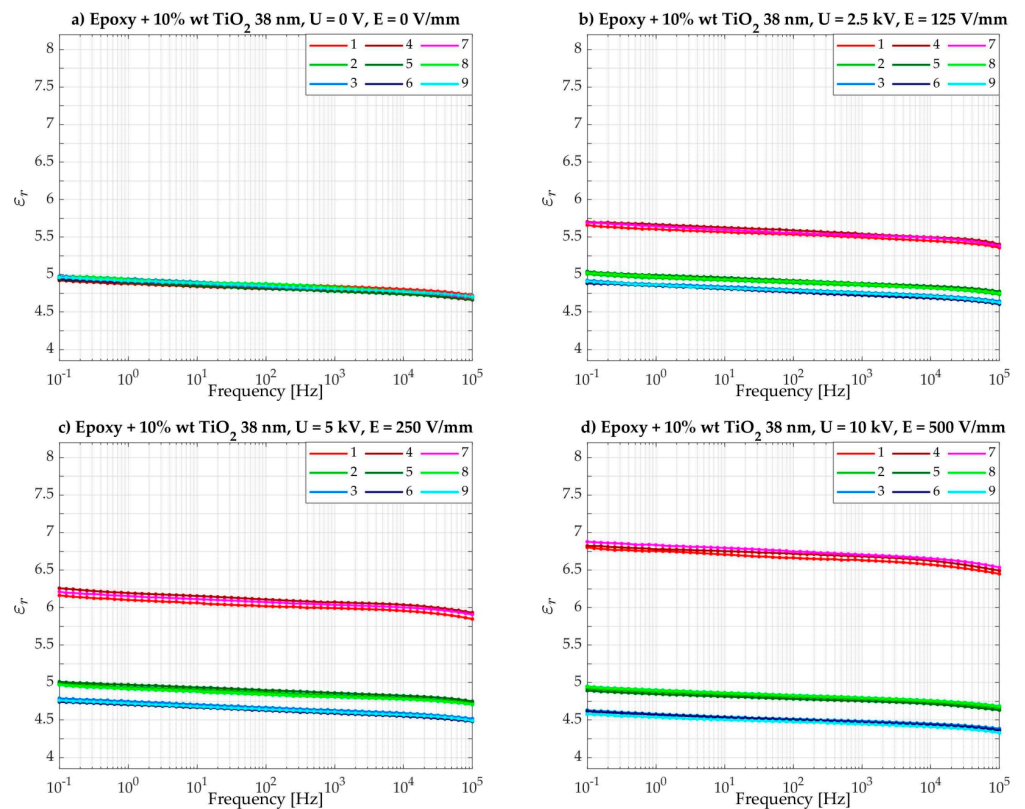


Figure 13. Broadband characteristics of ϵ_r for samples with TiO_2 38 nm filler. Applied electric field stress E_{av} : (a) $0.0 \text{ V}\cdot\text{mm}^{-1}$, (b) $125 \text{ V}\cdot\text{mm}^{-1}$, (c) $250 \text{ V}\cdot\text{mm}^{-1}$, and (d) $500 \text{ V}\cdot\text{mm}^{-1}$.

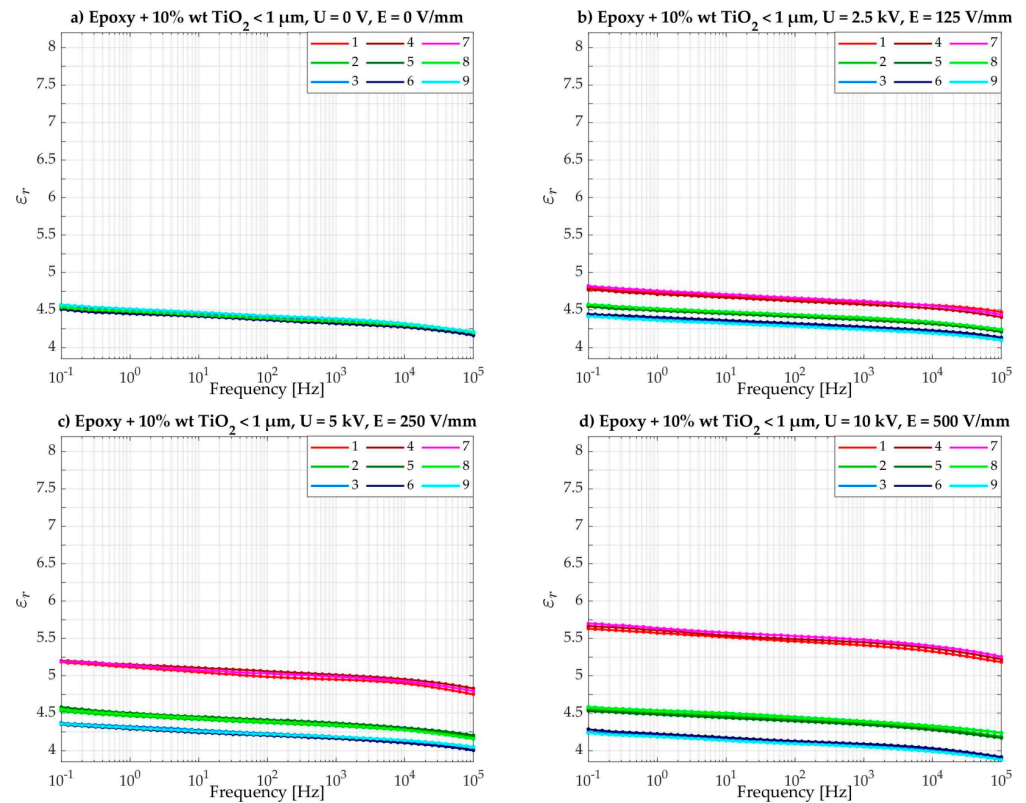


Figure 14. Broadband characteristics of ϵ_r for samples with $\text{TiO}_2 < 1 \mu\text{m}$ filler. Applied electric field stress E_{av} : (a) $0 \text{ V}\cdot\text{mm}^{-1}$, (b) $125 \text{ V}\cdot\text{mm}^{-1}$, (c) $250 \text{ V}\cdot\text{mm}^{-1}$, and (d) $500 \text{ V}\cdot\text{mm}^{-1}$.

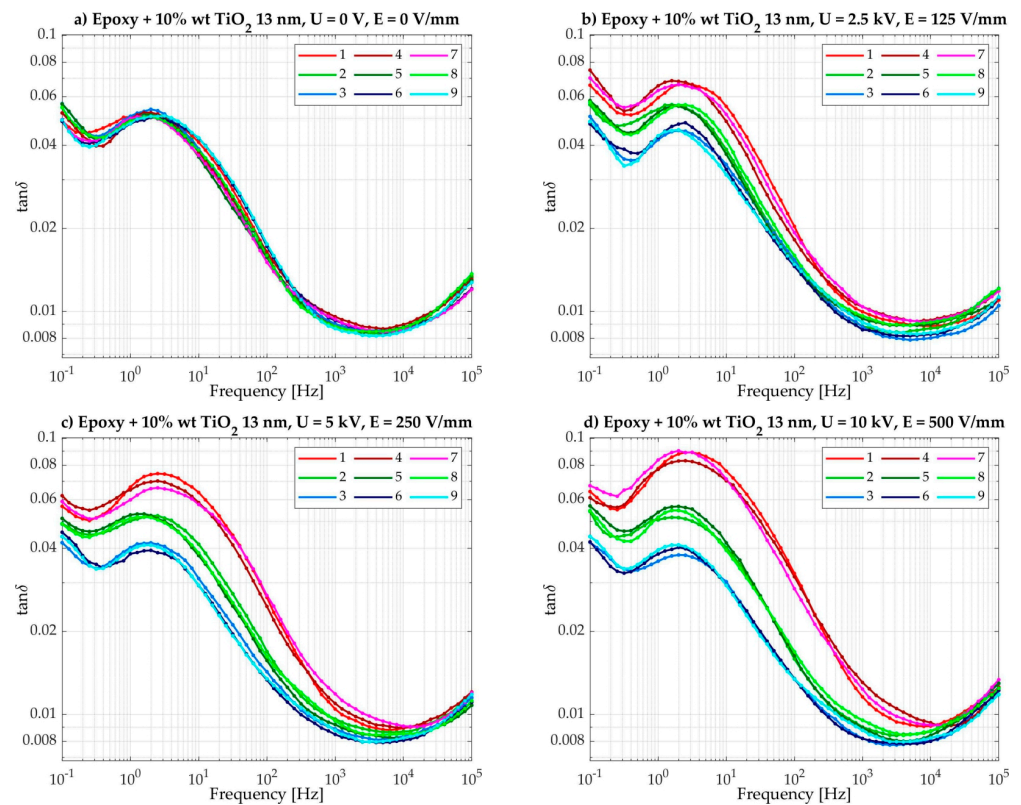


Figure 15. Broadband characteristics of $\tan\delta$ for samples with $\text{TiO}_2 13 \text{ nm}$ filler. Applied electric field stress E_{av} : (a) $0 \text{ V}\cdot\text{mm}^{-1}$, (b) $125 \text{ V}\cdot\text{mm}^{-1}$, (c) $250 \text{ V}\cdot\text{mm}^{-1}$, and (d) $500 \text{ V}\cdot\text{mm}^{-1}$.

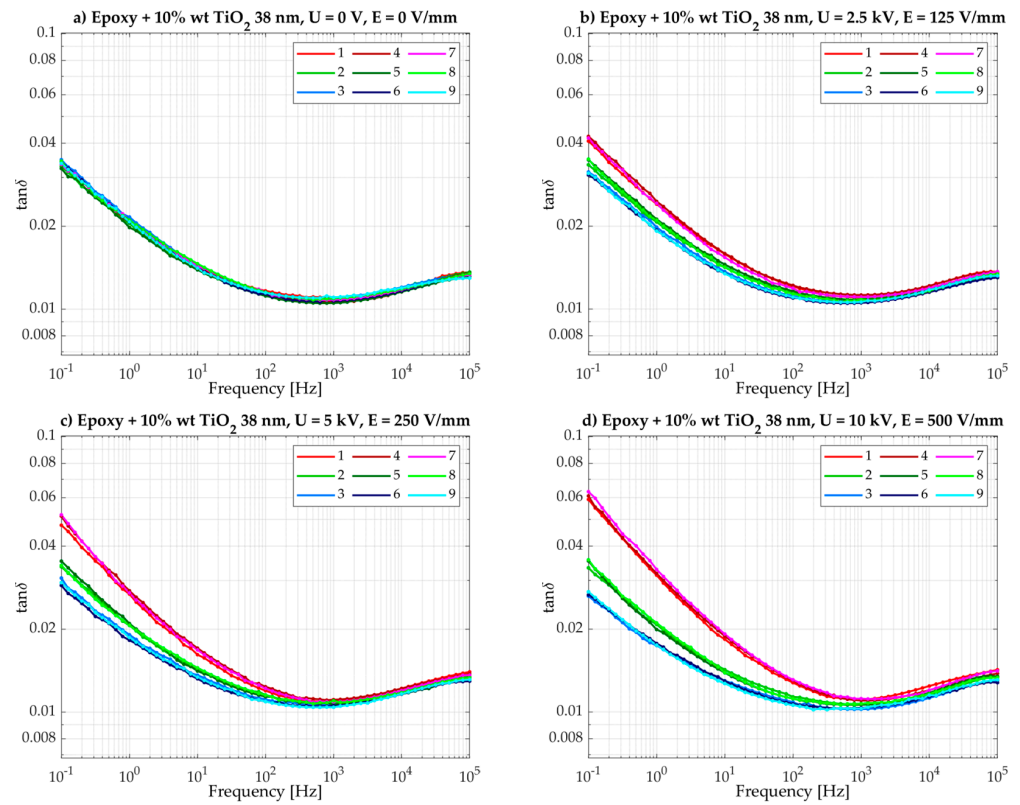


Figure 16. Broadband characteristics of $\tan\delta$ for samples with TiO_2 38 nm filler. Applied electric field stress E_{av} : (a) $0 \text{ V}\cdot\text{mm}^{-1}$, (b) $125 \text{ V}\cdot\text{mm}^{-1}$, (c) $250 \text{ V}\cdot\text{mm}^{-1}$, and (d) $500 \text{ V}\cdot\text{mm}^{-1}$.

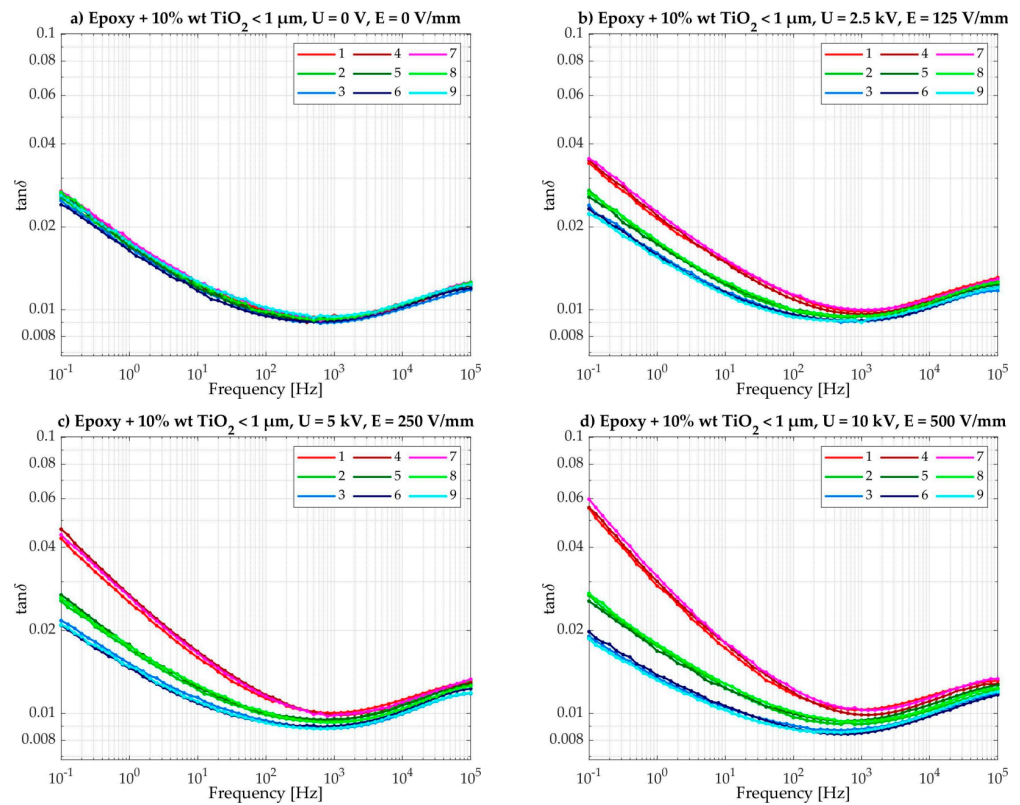


Figure 17. Broadband characteristics of $\tan\delta$ for samples with $\text{TiO}_2 < 1 \mu\text{m}$ filler. Applied electric field stress E_{av} : (a) $0 \text{ V}\cdot\text{mm}^{-1}$, (b) $125 \text{ V}\cdot\text{mm}^{-1}$, (c) $250 \text{ V}\cdot\text{mm}^{-1}$, and (d) $500 \text{ V}\cdot\text{mm}^{-1}$.

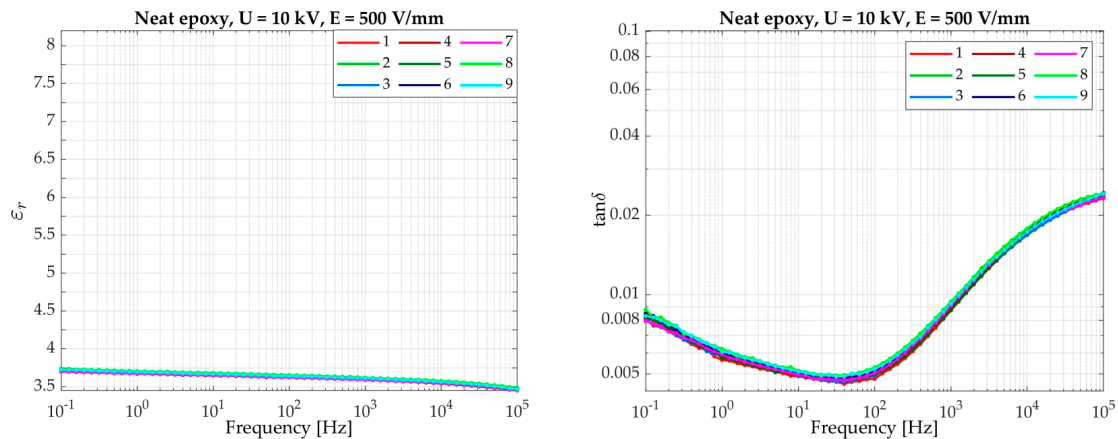


Figure 18. Broadband characteristics of ϵ_r (left) and $\tan\delta$ (right) for samples made of neat epoxy resin. Applied electric field stress $E_{av} = 500 \text{ V}\cdot\text{mm}^{-1}$.

For all reference samples made of neat epoxy resin at the four E_{av} values applied during the experiment, no differences were recorded between the broadband characteristics of the dielectric constant and the dielectric loss tangent. The characteristics presented in Figure 18, for samples processed at an average electric field stress of $500 \text{ V}\cdot\text{mm}^{-1}$, are the same for samples manufactured at other values of electric field, i.e., at $0.0 \text{ V}\cdot\text{mm}^{-1}$, $125 \text{ V}\cdot\text{mm}^{-1}$, and $250 \text{ V}\cdot\text{mm}^{-1}$. The dielectric constant of the neat epoxy resin decreases monotonically from 3.73 to 3.48 in the frequency range from 10^{-1} Hz to 10^5 Hz . The dielectric loss factor reaches a minimum (<0.005) in the frequency decade from 10 Hz to 100 Hz. This parameter increases for frequencies lowered from 10 Hz to 0.1 Hz and for frequencies increased from 100 Hz to 100 kHz, where it has its highest value.

4. Analysis and Discussion of Results

The use of TiO_2 particles (with three different sizes: 13 nm, 38 nm, and $<1 \mu\text{m}$) as a 10 wt% filler in the base epoxy resin increases the value of the dielectric constant of the obtained composite compared to its value for neat epoxy resin, in the entire range of analyzed frequencies (Figures 12a, 13a, 14a, and 18 and Tables 2–4). The increase in dielectric constant is the highest for the 13 nm nanofiller (Figure 12a, Table 2) and the lowest for the filler with particles $<1 \mu\text{m}$ (Figure 14a, Table 4). The presence of nanofiller particles causes two opposing effects in the cross-linked structure of the base polymer. On the one hand, they reduce the mobility of the main-chain moieties and branch/chain ends of the base polymer, which ultimately leads to a lower value of the dielectric constant. On the other hand, they cause the accumulation of additional charges due to the interphase effect of the filler particles dispersed in the volume of the resin [71,94–97]. For low filling levels (low wt%) the first effect dominates, so the ability of the composite structure to accumulate charges decreases and the dielectric constant is lowered [95–98]. However, for the TiO_2 filler content of 10 wt% used in the experiment, the second effect is dominant, which causes the permittivity of the composite to be significantly higher than that of neat resin [90,94,95,97,98]. The differences in the dielectric constant between the three analyzed composites result from the different concentrations of TiO_2 particles in the epoxy composite volume (the number of particles is proportional to $1/r^3$) and the different filler specific surface area (SSA), which is characteristic of the individual filler dispersed in the resin. Reducing the filler particle size leads to an increase in the SSA value [99].

Table 2. Average values of $\varepsilon_r/\Delta\varepsilon_r$ and $\tan\delta$ at 50 Hz for samples filled with 10 wt% TiO₂ 13 nm.

$E_{av}, V \cdot mm^{-1}$	500		250		125		0	
Parameter	$\varepsilon_r/\Delta\varepsilon_r$	$\tan\delta$	$\varepsilon_r/\Delta\varepsilon_r$	$\tan\delta$	$\varepsilon_r/\Delta\varepsilon_r$	$\tan\delta$	ε_r	$\tan\delta$
Area: ①, ④, ⑦	7.28/39.7%	0.0418	6.59/26.5%	0.0359	6.03/15.7%	0.0258	5.21	0.0218
Area: ②, ⑤, ⑧	5.18/−0.6%	0.0219	5.14/−1.3%	0.0216	5.20/−0.2%	0.0197		
Area: ③, ⑥, ⑨	4.73/−9.2%	0.0168	4.85/−6.9%	0.0170	4.98/−4.4%	0.0186		

Table 3. Average values of $\varepsilon_r/\Delta\varepsilon_r$ and $\tan\delta$ at 50 Hz for samples filled with 10 wt% TiO₂ 38 nm.

$E_{av}, V \cdot mm^{-1}$	500		250		125		0	
Parameter	$\varepsilon_r/\Delta\varepsilon_r$	$\tan\delta$	$\varepsilon_r/\Delta\varepsilon_r$	$\tan\delta$	$\varepsilon_r/\Delta\varepsilon_r$	$\tan\delta$	ε_r	$\tan\delta$
Area: ①, ④, ⑦	6.72/38.6%	0.0142	6.08/25.4%	0.0131	5.57/14.8%	0.0127	4.85	0.0120
Area: ②, ⑤, ⑧	4.82/−0.6%	0.0118	4.88/0.6%	0.0121	4.92/1.4%	0.0120		
Area: ③, ⑥, ⑨	4.51/−7.0%	0.0112	4.66/−3.9%	0.0115	4.79/−1.2%	0.0116		

Table 4. Average values of $\varepsilon_r/\Delta\varepsilon_r$ and $\tan\delta$ at 50 Hz for samples filled with 10 wt% TiO₂ < 1 μm.

$E_{av}, V \cdot mm^{-1}$	500		250		125		0	
Parameter	$\varepsilon_r/\Delta\varepsilon_r$	$\tan\delta$	$\varepsilon_r/\Delta\varepsilon_r$	$\tan\delta$	$\varepsilon_r/\Delta\varepsilon_r$	$\tan\delta$	ε_r	$\tan\delta$
Area: ①, ④, ⑦	5.51/24.9%	0.0132	5.04/14.3%	0.0126	4.65/5.4%	0.0120	4.41	0.0104
Area: ②, ⑤, ⑧	4.44/0.7%	0.0105	4.41/0.0%	0.0104	4.43/0.5%	0.0106		
Area: ③, ⑥, ⑨	4.12/−6.6%	0.0092	4.23/−4.1%	0.0097	4.32/−2.0%	0.0100		

Tables 2–4 summarize the average values of ε_r and $\tan\delta$ at 50 Hz, calculated for three characteristic areas, i.e., at the anode, at half the sample width, and at the cathode (for location of the areas, see Figure 5). For the dielectric constant, the relative increases in its average value, as a result of the electrophoresis process in relation to ε_r of specimens from the reference groups (marked in green), were determined for each size of TiO₂ particles:

$$\Delta\varepsilon_r = \frac{\varepsilon_r@E_{av} - \varepsilon_r@0.0 \text{ V/mm}}{\varepsilon_r@0.0 \text{ V/mm}} \times 100\% \quad (6)$$

The characteristics of ε_r and $\tan\delta$ at measurement areas 1 to 9 in each group of samples not exposed to the E field are in good agreement. This indicates a uniform dispersion of TiO₂ particles in the epoxy resin obtained in the process of mechanical mixing of the composite components. The analysis of changes in the dielectric constant value shows that in all composite samples, made on the basis of epoxy resin filled with TiO₂ particles of three different sizes (13 nm, 38 nm, and <1 μm), subjected to an external electric field E , the anaphoresis process takes place. This means that after mechanical mixing of the composite components, the filler particles suspended in the liquid resin have a negative charge (anions) and, under the influence of the E field, an electrophoretic force acts on them, stimulating their movement towards the electrode with a positive potential (anode) [55]. As a result, when the resin mixture is still liquid and at the gelation stage, when the curing process is developing, charge and mass transport processes take place in the resin, gradually changing the concentration of TiO₂ particles in the sample volume. The obtained modification of the local value of the dielectric constant ε_r and the dielectric loss factor $\tan\delta$ depends on the size of TiO₂ particles and their concentration. Assuming that the filler particles are spherical, taking into account (2) and (3), the velocity v of their transport in the suspending medium can be determined by the following formula:

$$v = \mu_{ep}E = \frac{q}{r} \frac{1}{6\pi\eta} E \quad (7)$$

In the described electrophoretic process, carried out in the epoxy composite in the initial stages of curing after mixing the components, the velocity v of the TiO_2 particles is not constant and depends on three factors:

- (a) The ratio q/r , i.e., two basic parameters describing the individual characteristics of a charged particle migrating in the suspending medium under the influence of electrophoretic force;
- (b) Properties of the suspending medium (i.e., cross-linking epoxy resin), characterized by a viscosity coefficient η that changes dynamically during the electrophoresis process;
- (c) The value of the electric field strength E forcing the movement of charged particles in the suspending medium.

The radii r of filler particles exhibit some statistical dispersion. This remark also applies to the particle charge, which means that the ratio q/r in a set of particles is not a constant value. However, it should be noted that this is not the only reason why the migration velocities of TiO_2 particles are different. An analysis of formula (7), taking into account electrothermal phenomena and stages of the curing process occurring in the sample material when the electric field E is present, indicates that the transport of filler particles is a multiparametric, nonstationary, and nonlinear process. This is because the velocity of an individual particle depends on the time elapsed since the resin was mixed with the hardener, the temperature, and the particle's location in the sample material. The particle velocity v is influenced by electrophoretic mobility μ_{ep} and the local electric field strength E . The electrophoretic mobility of particles is affected not only by the ratio q/r but also by the local viscosity η of the suspending medium. In the case of the electrophoretic process occurring in epoxy resin after mixing with the hardener, the local viscosity is a complex function of time and temperature, $\eta = f(t, T)$. In practice, this function is challenging to precisely describe due to the complex kinetics of the curing process reactions, leading to the gradual formation of chains, branches, and a fully cross-linked polymer structure [67–69,100,101]. The resin cross-linking process causes significant changes over time in its physical parameters, including viscosity η . During electrophoresis, an additional factor influencing the rate of resin curing is the Joule heat generated within the sample volume as a result of applying the U_{DC} voltage. This voltage creates an electric field E between the electrodes and causes a time-varying current $i(t)$ through the sample.

The measured current $i(t)$ is the result of several physical processes occurring in the sample material after applying the U_{DC} voltage. The components of this current are the following:

1. Pulse current $i_C(t)$ charging the geometric capacitance of the sample, flowing for a very short time, just after increase in voltage on the electrodes to the U_{DC} value. Its maximum value is limited by the current capacity of the voltage source.
2. Conduction current $i_\sigma(t)$, conditioned by the value of the time-varying bulk conductivity $\sigma(t)$ of the composite. The conductivity component of the current is of the ionic type and is strongly dependent on temperature. In the progressing curing process, it also depends on the degree of cross-linking of the polymer structure of the composite and the influence of filler particles.
3. Polarization current $i_p(t)$ resulting from polarization processes occurring in dielectric under the influence of an external electric field. The waveform of this current is also influenced by the phase transformations of the composite material and the formation of the cross-linked polymer structure of the sample.
4. Electrophoretic current $i_{ep}(t)$, related to the displacement of charged TiO_2 filler particles in the suspension medium. This current is a small part of the conduction current flowing through the composite when U_{DC} voltage is present between the external electrodes.

The analysis of the results depicted in Figures 6a and 7a suggests that, depending on the applied voltage and the size of the TiO_2 filler particles, the peak value and dynamics of the current profile exhibit variations. It is known that changes in the resistance of epoxy

resin during the curing process correlate well with changes in its viscosity in time before the gelation phase [100,101]. The resistance is inversely proportional to the current flowing through the cured epoxy composite, so at the highest current values the lowest resistance values occur, and then the viscosity of the resin is also the lowest. Under these conditions, TiO_2 particles subjected to electrophoretic forces are transported through the resin with the least resistance. For the composite with TiO_2 filler particles $<1 \mu\text{m}$, the current peak occurs earlier and reaches a higher magnitude than in the case of neat resin. Next, the rate of current reduction after reaching its peak is more pronounced compared to neat resin. In the case of TiO_2 nanofillers (13 nm and 38 nm), the peak current values are clearly lower than for the neat resin, and the 38 nm particles cause a greater reduction in conductivity at the peak current. However, the decrease in current values after reaching the peak is slower. In both cases, this is related to temperature. Heating the sample to a higher temperature accelerates the curing process, leading to a faster formation of the network structure of the polymer and a quicker increase in sample resistance and resin viscosity [100–102]. As a result, at this stage of the process, characterized by negative feedback, the production of Joule heat decreases, ultimately leading to the immobilization of filler particles in the composite structure. For nanoscale TiO_2 filler, when a lower current flows through the sample (compared to the current for neat epoxy resin), the heating of the composite is less intense, and the resin curing process takes longer.

The total electric charge Q that flows through the composite sample over time t from the moment the DC voltage U_{DC} is applied to the electrodes ($t = 0$) can be determined by the following formula:

$$Q(t) = \int_0^t i(t) dt \quad (8)$$

At the same fixed U_{DC} voltage, the change in charge $Q(t)$ and the total charge that has flowed during the entire electrophoresis process, i.e., $Q(t_{\text{max}})$ (in the described experiment, $t_{\text{max}} = 3600 \text{ s}$), depend on the size of TiO_2 filler particles (Figure 19a). The fastest change in charge was observed for the composite with TiO_2 particles $<1 \mu\text{m}$ (highest peak current and highest temperature, thus accelerating the curing process), and the largest charge $Q(t_{\text{max}})$ flowed in the composite with the smallest filler particle size, 13 nm. Reducing the U_{DC} voltage (and thus the electric field intensity E) decreases the dynamics of the charge change $Q(t)$ and affects the value of $Q(t_{\text{max}})$. Although $Q(t_{\text{max}})$ for composite samples with $\text{TiO}_2 <1 \mu\text{m}$ is almost the same for U_{DC} voltages of 10 kV and 5 kV (Figure 19b), the obtained changes in dielectric parameters for both groups of composite samples are clearly different (Figure 14c,d and Figure 17c,d).

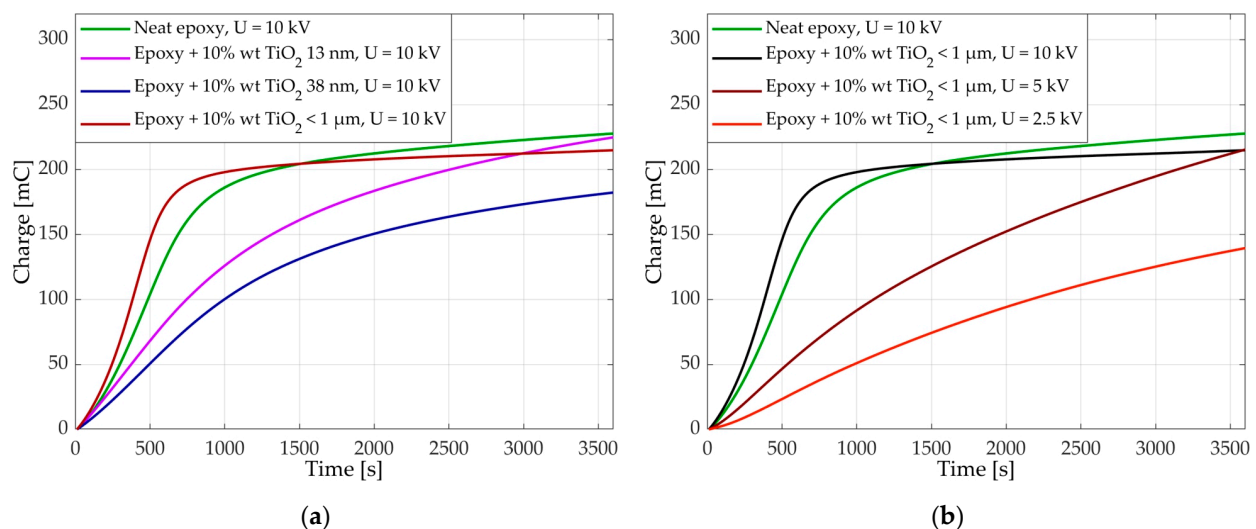


Figure 19. Changes in $Q(t)$ during the application of U_{DC} voltage to the curing sample: (a) constant U_{DC} voltage, various sizes of TiO_2 filler particles; (b) TiO_2 filler $<1 \mu\text{m}$, various values of U_{DC} voltage.

Larger changes in dielectric constant and $\tan\delta$ occur in samples subjected to a higher electric field. This indicates that the electrophoretic transport of TiO_2 filler particles is not efficiently realized throughout the entire flow of electric charge $Q(t)$. This is a result of the epoxy resin curing process; after reaching the minimum sample resistance and resin viscosity, the latter parameter dynamically increases, unlike electrical resistance [100,101].

As indicated by Equation (7), one of the factors influencing the transport velocity of TiO_2 filler particles in the resin is the electric field. For DC voltage, the distribution of the electric field E in the resin is mainly determined by electrical conductivity. In the absence of a temperature gradient, the distribution of the electric field E in the region between the electrodes is uniform. The generation of Joule heat within the volume of the resin necessitates considering the presence of a nonuniform temperature field when analyzing the influence of the electric field E on the electrophoresis process, confirmed by observations of the thermal state of the sample surfaces (Figures 8–11). To achieve this, an analysis of the electric field distribution was conducted using a numerical model in the COMSOL Multiphysics 6.2 program, taking into account changes in electrical conductivity σ of the resin with the application of the empirical Formula (9) [103]:

$$\sigma(T, E) = \sigma_0 \cdot \exp(\alpha \cdot T) \cdot \exp(\beta \cdot E) \quad (9)$$

where

- σ_0 —material conductivity, $\text{S} \cdot \text{m}^{-1}$ (at $E = 0.0 \text{ V} \cdot \text{m}^{-1}$ and $T = 0 \text{ }^\circ\text{C}$);
- T —temperature, $^\circ\text{C}$;
- E —electric field strength, $\text{V} \cdot \text{m}^{-1}$;
- α —temperature factor of conductivity, $^\circ\text{C}^{-1}$;
- β —field factor of conductivity, $\text{V}^{-1} \cdot \text{m}$.

Due to the relatively low E_{av} values (max. $500 \text{ V} \cdot \text{mm}^{-1}$), the influence of the field factor, represented in Formula (9) by the β parameter, was not taken into account in the numerical simulations. Changes in the conductivity of the epoxy resin $\sigma(\alpha \cdot T, t)$ were defined in numerical simulations in such a way that the current flowing in the simulation model (Figure 20a) reflects the real current waveform $i(t)$, recorded during the experiment (Figure 6a). Table 5 contains the material parameters used to model the temperature and electric field distributions in the material sample (processed in the mold shown in Figure 2) subjected to the U_{DC} voltage. The value of the α parameter for the epoxy resin was estimated based on the test results presented in [104]; other material parameters were taken from [66] or from the library of typical material parameters of the COMSOL program.

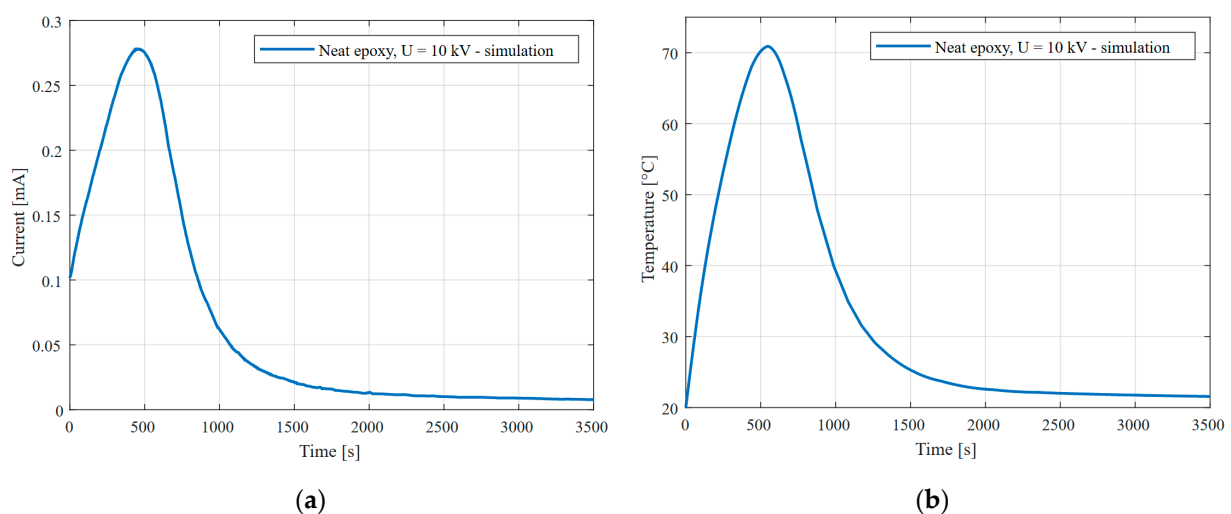


Figure 20. Numerically simulated waveforms: (a) current $i(t)$ flowing through the sample, and (b) temperature $T(t)$ at the central point of the neat epoxy sample; $U_{\text{DC}} = 10 \text{ kV}$.

Table 5. Material parameters used for E field numerical simulation.

Parameter	Value	Unit
Stainless steel		
Electrical conductivity, σ	4×10^6	$\text{S}\cdot\text{m}^{-1}$
Dielectric constant, ϵ_r	1	-
Heat capacity, C_p	475	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
Thermal conductivity, k	44.5	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
Density, ρ	7850	$\text{kg}\cdot\text{m}^{-3}$
Epoxy resin		
Electrical conductivity, σ	$\sigma(\alpha\cdot T, t)$	$\text{S}\cdot\text{m}^{-1}$
Dielectric constant, ϵ_r	4	-
Heat capacity, C_p	1380	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
Thermal conductivity, k	0.26	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
Density, ρ	1130	$\text{kg}\cdot\text{m}^{-3}$
Temperature factor of epoxy conductivity, α	0.1	K^{-1}
PTFE		
Electrical conductivity, σ	1×10^{-16}	$\text{S}\cdot\text{m}^{-1}$
Dielectric constant, ϵ_r	2	-
Heat capacity, C_p	1050	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
Thermal conductivity, k	0.24	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
Density, ρ	2200	$\text{kg}\cdot\text{m}^{-3}$
Ambience		
Heat transfer coefficient, h	10	$\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$
Ambient temperature, T_{amb}	20	$^{\circ}\text{C}$

Figure 20 depicts modeled trends of the current $i(t)$ flowing through a specimen made of neat resin at a voltage of 10 kV (Figure 20a) and the temperature change $T(t)$ at a point located at the center of the specimen surface (Figure 20b). The modeling results qualitatively accurately reflect the effect of time delay between the peak value of current and the maximum temperature value. During the electrophoresis process, due to heat transfer to the surroundings, an uneven temperature distribution arises in the specimen material. Exemplary 2D distributions of temperature T and electric field strength E , determined at the moment when the central point of the neat resin sample reaches the highest temperature under a DC voltage of 10 kV, are presented in Figure 21, and temperature T and electric field strength E profiles along the y -axis passing through the central point of the sample are shown in Figure 22.

The results of numerical simulations indicate that the electric field E , which influences the electrophoretic velocity of negatively charged TiO_2 filler particles, has the highest values near the electrodes. Considering Equation (7), the uneven distribution of electric field intensity between the electrodes affects the variation in electrophoretic particle velocities, depending on their positions. Consequently, it is expected that in each of the considered cases, the region near the anode will have the highest concentration of filler particles, while the region near the cathode will have the lowest. This conclusion aligns with the measurement results of dielectric constant obtained for all groups of samples.

As a result of each electrophoresis process carried out in a model system with a wide interelectrode gap (20 mm), an insulating system with gradually modified permittivity was achieved. The electrophoretic transport of TiO_2 particles led to an increase in the ϵ_r values, dependent on the filler particle size and the applied U_{DC} voltage (Figures 12–14). The highest ϵ_r values and the largest relative differences $\Delta\epsilon_r$ between the anodic and cathodic regions were recorded for the composite with TiO_2 nanoparticles of 13 nm, subjected to electrophoresis at 10 kV (Figure 12d). The weakest effect of this kind was observed for TiO_2 particles $< 1\ \mu\text{m}$. For 13 nm particles, a low-frequency dielectric polarization process (below 1 Hz) was also revealed, causing a significant increase in the loss factor $\tan\delta$ in the

frequency range between 1 Hz and 10 Hz for each of the considered cases (Figure 15). The 13 nm filler is characterized by the highest SSA value, so the effects related to interfacial interactions between the base polymer and TiO_2 nanoparticles are most pronounced for it. This creates conditions in the nanocomposite structure for the polarization process characteristic of interface systems [1,4,95,99,105].

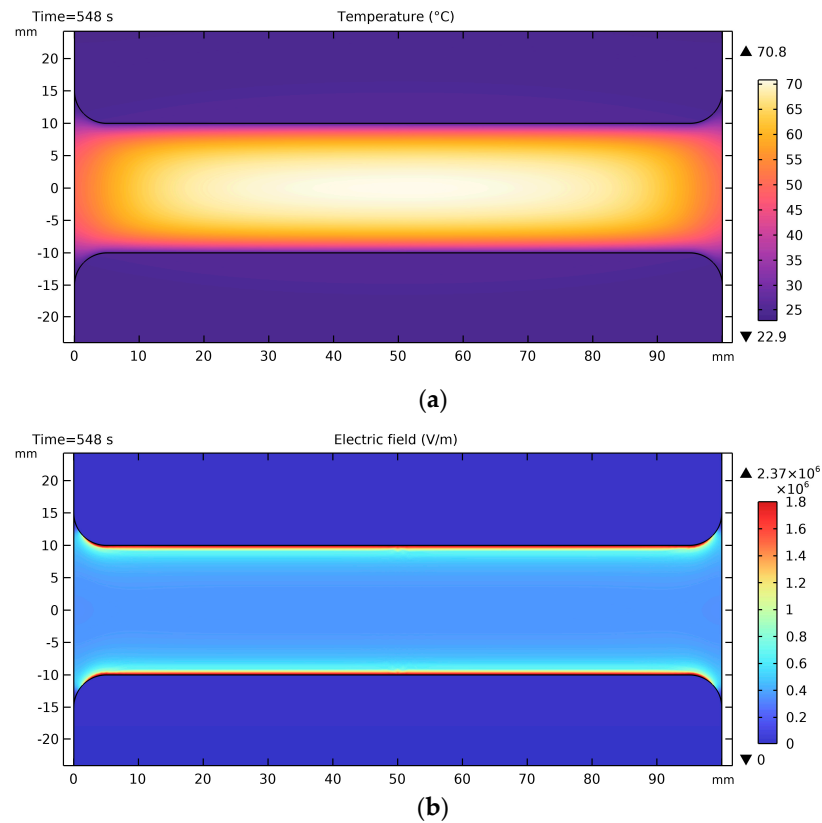


Figure 21. Numerically determined exemplary 2D distributions: (a) temperature field T , and (b) electric field E for a sample of neat epoxy; at $U_{DC} = 10$ kV and for the highest temperature at the central point.

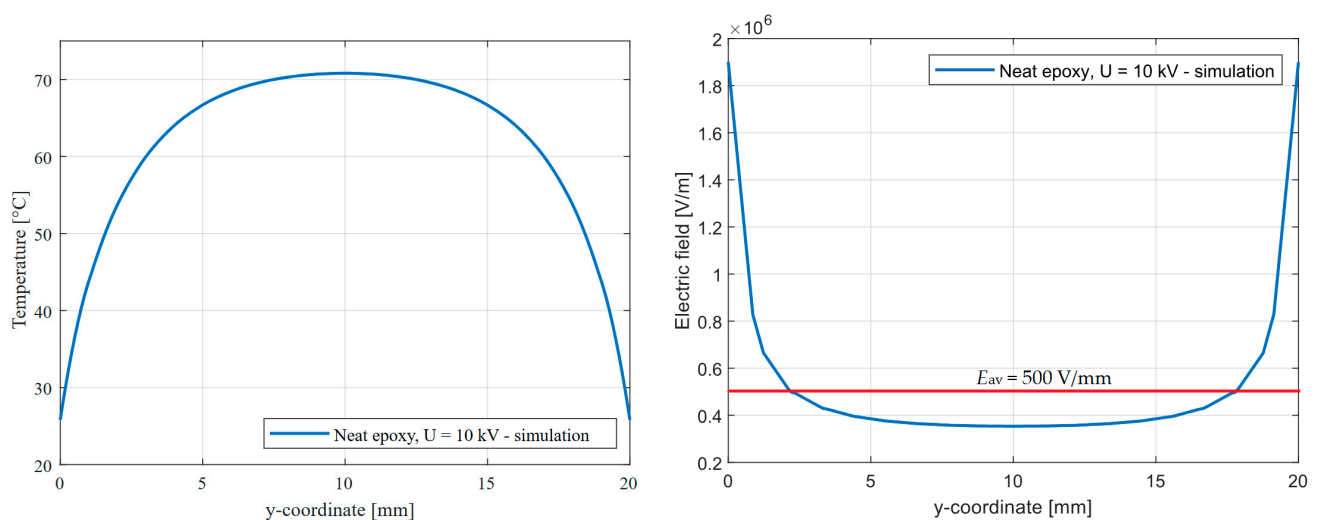


Figure 22. Numerically determined exemplary temperature T and electric field E profiles along the y -axis passing through the central point of the sample of neat epoxy; $U_{DC} = 10$ kV for the highest attained temperature at the central point.

For all samples of each investigated composite (i.e., for all sizes of TiO_2 particles), an increase in $\tan\delta$ was recorded for decreasing frequencies, below 100 Hz. This indicates an increasing contribution of conductivity losses in $\tan\delta$ value [97,106]. The increase in the loss factor is, in each case, greater for the anodic regions, characterized by a higher concentration of filler particles.

5. Conclusions

In the presented laboratory experiment, the possibility of producing FGM composite insulation systems with gradient-modified permittivity, based on epoxy resin with TiO_2 powder filler, was examined. To obtain a change in the concentration of filler particles, the electrophoresis method was employed. In this method, the transport processes of charged particles were stimulated under the influence of an external electric field E applied to the sample. The electric field was applied for a duration of 1 h, including the gelation time of the base resin after adding the hardener. The influence of two independent factors on the resulting gradient of permittivity in the insulating material samples was observed and analyzed:

- (1) The material factor, resulting from the use of TiO_2 filler particles of three different dimensions (13 nm, 38 nm, and $<1\ \mu\text{m}$);
- (2) The process factor resulting from the application of four different values of electric field stress in the material sample, i.e., $0.0\ \text{Vmm}^{-1}$ (without external E field) and with external E field ($125\ \text{Vmm}^{-1}$, $250\ \text{Vmm}^{-1}$ and $500\ \text{Vmm}^{-1}$), causing electrophoretic movement of filler particles, but also heating the material with Joule heat, resulting in an increase in the reaction kinetics responsible for the rate of the epoxy resin curing process.

In all groups of composite samples exposed to an external DC electric field E (regardless of the dimensions of the filler particles and the value of the E field), the effect of gradient-modified permittivity was found. In each case, the TiO_2 filler particles had a negative charge, so their electrophoretic transport resulted in an increase in the dielectric constant ϵ_r in the areas close to the anode. The increase in the ϵ_r value obtained in this way is greater for smaller filler particles and for higher values of the external electric field. The greatest difference in the value of the dielectric constant of the epoxy composite between the areas near the cathode and anode was obtained for the group of samples with TiO_2 particles of 13 nm, produced using a field $E = 500\ \text{Vmm}^{-1}$ (Figure 12d). The obtained results indicate that when producing ϵ -gradient epoxy materials using electrophoresis, a gentle or steeper change in this dielectric parameter can be achieved.

During the electrophoresis process, the current flowing through the sample generates Joule heat, raising the temperature of the composite mixture. Initially, for the mixture in the liquid phase, this reduces the viscosity of the resin and causes an increase in the mobility of charged filler particles. Subsequently, due to the thermally accelerated resin curing process, its viscosity quickly rises, ultimately immobilizing the particles in the structure of the base polymer. The conducted studies revealed that nanosized TiO_2 particles decrease the values of the current flowing through the sample, consequently limiting heat generation and the heating of the composite.

The temperature distribution in the electrophoretically processed composite modifies the distribution of electric field strength E in such a way that the highest values occur in the immediate vicinity of the electrodes.

In summary, the application of electrophoresis for gradient modification of permittivity in a resin-based insulating system with a relatively wide interelectrode gap is feasible. Proper planning of the procedure for creating such a system requires consideration of a series of factors, both material- and process-related. Some of these factors may lead to the occurrence of different or even mutually opposing effects at successive stages of the composite curing.

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