Lithuanian Journal of Physics, Vol. **57**, No. 2, pp. 103–111 (2017)

TEMPERATURE AND FREQUENCY DEPENDENCE OF THE DIELECTRIC AND PIEZOELECTRIC RESPONSE OF P(VDF–TrFE)/$CoFe_2O_4$ MAGNETOELECTRIC COMPOSITES

Š. Svirskas [a], J. Belovickis [a], D. Šemeliovas [a], P. Martins [b],

S. Lanceros-Méndez [b, c, d], and J. Banys [a]

[a] *Faculty of Physics, Vilnius University, Saulėtekio 9/3, LT-10222 Vilnius, Lithuania*
[b] *Department of Physics, University of Minho, 4710-057 Braga, Portugal*
[c] *BC Materials, Parque Científico y Tecnológico de Bizkaia, 48160-Derio, Spain*
[d] *IKERBASQUE, Basque Foundation for Science, Bilbao, Spain*
E-mail: sarunas.svirskas@ff.vu.lt; jaroslavas.belovickis@ff.vu.lt; daumantas.semeliovas@ff.stud.vu.lt; martins@fisica.uminho.pt; lanceros@fisica.uminho.pt; juras.banys@ff.vu.lt

Received 15 March 2017; revised 10 April 2017; accepted 20 June 2017

$CoFe_2O_4$ nanoparticles embedded in polyvinylidene fluoride–trifluoroethylene (P(VDF–TrFE)) matrix show suitable properties for practical applications as piezoelectric and magnetoelectric transducers. The knowledge about the dielectric and electromechanical responses of the multiferroic films in a broad frequency and temperature range is essential for applicability. The purpose of this work is to investigate the dielectric, ferroelectric and piezoelectric properties of multiferroic composites based on P(VDF–TrFE) as a host matrix and Co_2FeO_4 as a magnetic filler. Free-standing films with a different concentration of the filler were investigated. The polarization switching was demonstrated for all the compositions. The polarization displacement hysteresis was achieved at different temperatures. The piezoelectric coefficient d_{33} is not affected by different concentration of ferrite. On the other hand, the composition with the largest weight % of Co_2FeO_4 shows higher coercive fields which is not favourable for applications. This indicates that the optimal content of the filler must be determined and taken into account when optimizing both ferroelectric and magnetoelectric properties.

Keywords: polymer-matrix composites (PMCs), smart materials, electrical properties

PACS: 81.05.Lg, 81.07.Bc, 77.55.Nv

1. Introduction

Over the past decade, multiferroic materials and their applications are one of the main research topics in the field of ferroics. Such materials have a huge potential for the next generation multifunctional devices [1–3]. These systems show a simultaneous existence of two or more ferroic orders, and a cross-coupling between them. The coupling can appear between magnetic spins, polarization, ferroelasticity and even ferrotoroidicity [1].

Single-phase materials with strong cross-coupling properties are desired although they are rare in nature. Moreover, coupling appears only at low temperatures, which reduces applicability of such materials [4].

The composite approach offers a large potential for technological optimization due to many degrees of freedom in the device design, such as the choice of piezoelectric and magnetostrictive materials, their simple production process, and their three-dimensional arrangement [5]. This magnetoelectric (ME) product property leads to output signals at room temperature many orders of magnitude higher than in a single-phase materials and therefore is very attractive for technological applications such as magnetic field sensors, nonvolatile memory elements, ferroelectric photovoltaics, nanoelectronic and biomedical fields [1, 6, 7].

Multilayer magnetostrictive/piezoelectric thin films as well as bulk or laminate composite materials have attracted growing attention due to their high ME coupling. However, these laminated and ceramic composites have some limitations such as low resistivity and high dielectric losses which make them not so viable for device miniaturization and fabrication [4, 8, 9]. Furthermore, to simplify the preparation process as well as to avoid the problem of inter-diffusion between the piezoelectric and magnetostrictive phases, it is also important to select materials, which require significantly lower processing temperatures [9]. In this context, polymer based ME nanocomposites which can overcome the flaws of the abovementioned structures are an interesting, challenging and innovative research field and most probably will bridge the gap between fundamental research and applications in the near future [8, 10]. In these ME nanocomposites, where magnetostrictive nanoparticles are introduced in a piezoelectric polymer matrix, the mechanical deformation of the magnetostrictive phase results in polarization variations in the piezoelectric phase [11].

Polyvinylidene fluoride (PVDF) and its copolymers are the most suitable for the preparation of ME composites since they possess the largest dielectric constant and piezoelectric response among polymers [8, 12]. Additionally, due to the chemical inertness, PVDF-based materials are suitable for applications in relatively harsh conditions [13].

Concerning the magnetostrictive phase of polymer-based ME composites, $CoFe_2O_4$ has been preferably used due to its large magnetostrictive coefficients, high Curie temperature and chemical stability 14, 15]. Resulting from these interesting properties, the high ME coupling of ferrite–PVDF composites has been already reported and often discussed [2, 14–16].

It is crucial for applications to study dielectric and ferroelectric properties of nanocomposites vs external stimuli (i.e. frequency and temperature) because these properties determine the performance of ME materials in telecommunications, electronics, biomedicine and some other fields [13, 17]. No previous studies can be found in the literature regarding the temperature dependences of those responses of $CoFe_2O_4$/P(VDF–TrFE) nanocomposites.

In this work, the preparation of $CoFe_2O_4$/P(VDF–TrFE) nanocomposites with a high dielectric permittivity and an enhanced ferroelectricity/piezoelectricity is reported. Additionally, the influence of ferrite content, frequency and temperature on such properties is presented.

2. Experiment

P(VDF–TrFE) powder was obtained from *Solvay Solexis*, $CoFe_2O_4$ nanoparticles (35–50 nm) were purchased from *Nanoamor* and N,N-dimethylformamide (DMF) pure grade solvent was purchased from *Fluka*.

$CoFe_2O_4$/PVDF nanocomposites with $CoFe_2O_4$ content ranging from 5 to 11 weight percentage (wt.%) were prepared with an addition of cobalt ferrite nanoparticles into DMF and placing the mixture in an ultrasonic bath for 8 hours. Such ferrite contents have been chosen due to their high piezoelectric and ME responses [14, 15]. P(VDF–TrFE) powder was then added and its solution was mixed using a Teflon mechanical stirrer in the ultrasonic bath until the polymer was completely dissolved. Films were obtained by spreading the solution on a clean glass substrate. The solvent evaporation was achieved by heating the films (10 minutes) in an oven at 210 °C. Consequent cooling to room temperature (≈25 °C) led to polymer crystallization. Thus, free-standing flexible films (≈50 μm) were obtained by detaching from the glass substrate.

Dielectric characterization of P(VDF–TrFE)/$CoFe_2O_4$ nanocomposites was performed using two different experimental techniques. The investigation in the 20 Hz – 1 MHz frequency range was performed with a HP-4284A LCR meter. The capacitance and loss tangent (tan δ) were measured. The complex dielectric permittivity was calculated according to the parallel plate capacitor model.

At frequencies above 1 MHz, the inductance of the conventional measurement setup becomes important and cannot be neglected. Thus, the measurements at 1 MHz – 1 GHz frequencies were performed with an *Agilent* 8714ET vector network analyser. The samples were placed at the end of the coaxial line and the complex reflection coefficient was measured. The complex dielectric permittivity can be obtained according to the transmission line theory.

Dielectric data was measured in the 150–400 K interval. Keithley Integra 2700 multimeter equipped with either a T type thermocouple or a 100 Ω platinum resistor was used to measure the temperature.

Polarization and displacement hysteresis loops were measured with an *aixACCT* TF2000 system with external voltage supply up to 4 kV. To obtain polarization hysteresis, the current was measured, and after integration, the polarization was obtained. The displacement was measured by a single beam interferometer. All the experiments were carried out at temperatures from 200 to 400 K.

3. Results and discussion

In order to understand the underlying relaxation behaviour in the produced multiferroic nanocomposites, isothermal frequency dependent measurements at different temperatures (Fig. 1) were performed. Such experimental data reveals whether the degradation of the electrical properties of a polymer matrix occurs. The degradation might manifest in several cases in frequency dependences. The most common and most frequently encountered sign is an increase of the electrical conductivity. For particular applications, the increase of conductivity is desirable, but in our case, it could be considered as degradation because the aim of this work is to produce the composites for piezoelectric and magnetic applications. It is known that in ceramic–ferrite composites (i.e. $BaTiO_3$–$NiFe_2O_4$ [18]) the electrical conductivity varies quite drastically with respect to the concentration of ferrite. The largest effect is usually observed at lower frequencies. In our case the imaginary part of complex dielectric permittivity (which is related to conductivity) at room temperature does not show increase with the decrease of frequency. The same tendency is observed for all the investigated samples where the value of dielectric losses (the imaginary part of complex dielectric permittivity) remains the same. Furthermore, the real part of complex dielectric permittivity shows only a slight increase that might be related to a particular relaxation of a polymer matrix. The Maxwell–Wagner relaxation appears only at elevated temperatures. Most likely, it is related to the electrode–composite interface and is not an internal property of nanocomposites. Thus we can strongly state that the conductivity of our composites is not affected by different filler concentration.

An important issue is the dispersion of fillers in the polymer matrix. The homogeneity of the fillers can be reflected in dielectric spectra as well. PVDF–TrFE has the well-known relaxation which is related to the micro Brownian cooperative motions of the main chain backbone and is a dielectric manifestation of the glass transition temperature of PVDF and PVDF–TrFE copolymers [19–21]. In addition, earlier works showed that the crystallinity content of PVDF-based composites varies with the filler type and content [22]. One would expect that the dynamics of such

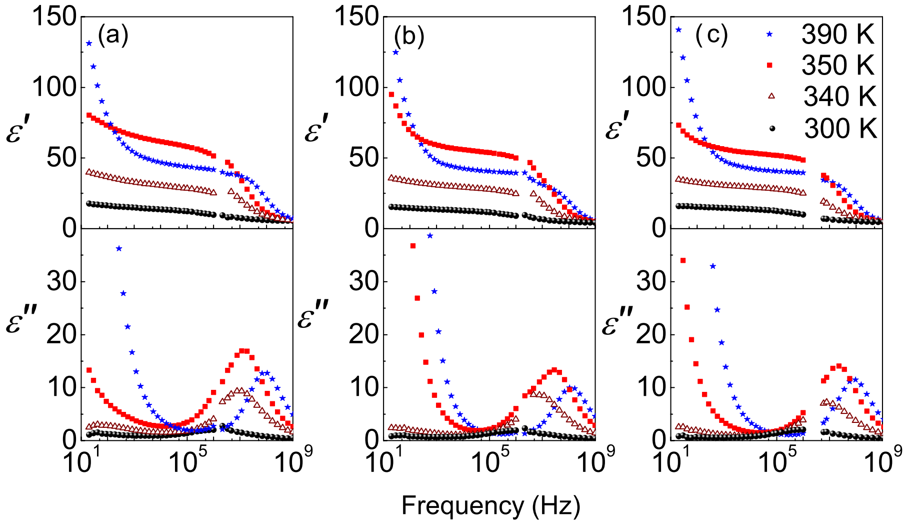

Fig. 1. Frequency dependence of the complex dielectric permittivity of nanocomposites with $CoFe_2O_4$ content of (a) 5 wt.%, (b) 7 wt.% and (c) 11 wt.%.

systems should alter as well. Again, that is not our case because the characteristic frequency (i.e. frequency at which the imaginary part of dielectric permittivity has maximum) is nearly the same for all investigated nanocomposites at different temperatures.

The only difference which can be observed is the value of static dielectric permittivity of nanocomposites. But it is only visible at higher temperatures. In order to clearly illustrate the difference, the temperature dependences at different frequencies are depicted in Fig. 2. The temperature region 150–350 K has concentration independent dielectric permittivity. The distinction between the investigated nanocomposites appears above 350 K. This behaviour can merely be explained by the effective medium theory. It is known that the permittivity of ferrites is of order 10. At lower temperatures PVDF–TrFE has the dielectric permittivity comparable to that of cobalt ferrite, thus the effective permittivity of the composite is the same despite the filler concentration. The drastic increase of the permittivity of PVDF–TrFE vs temperature leads to the change of the effective permittivity. This is clearly seen above 350 K – the nanocomposite with the largest concentration of cobalt ferrite has the lowest permittivity. This effect is observed in all frequencies.

Finally, all the P(VDF–TrFE)–$CoFe_2O_4$ composites under investigation have the same characteristic anomalies which are purely related to the PVDF–TrFE matrix. These broad dielectric loss peaks below 300 K (Fig. 2) are known as the β-relaxation process [19–21] and usually referred to the glass transition of P(VDF–TrFE) copolymer. The behaviour of this anomaly is characteristic of the ones observed in semicrystalline polymers [21]. In contrast to that, in polymers like polydimethylsiloxane (PDMS) this dynamic glass behaviour is referred to as a primary α relaxation, due to a relatively large-scale cooperative motion of many backbone segments in the amorphous phase [23, 24]. It also exhibits the Vogel–Fulcher freezing. The dielectric dispersion of the imaginary part of complex dielectric permittivity has been observed in the P(VDF–TrFE) based composites below (Fig. 2(a, b)) and above (Fig. 2(c)) their Curie temperature (350 K), the temperature of the second anomaly. This is the ferroelectric phase transition of the first order. It is clearly visible that no significant temperature shifts of the anomalies exist in the data of different composites. This data hints that ferroelectric properties of PVDF–TrFE are not hindered by ferrite inclusions.

Electric field dependent polarization (E-P) and electric field dependent displacement-(E-D) hysteresis loops were measured at 1 Hz on all the samples (Fig. 3). Distinct loops were observed for different composite films due to the variations in the content of $CoFe_2O_4$ nanoparticles on

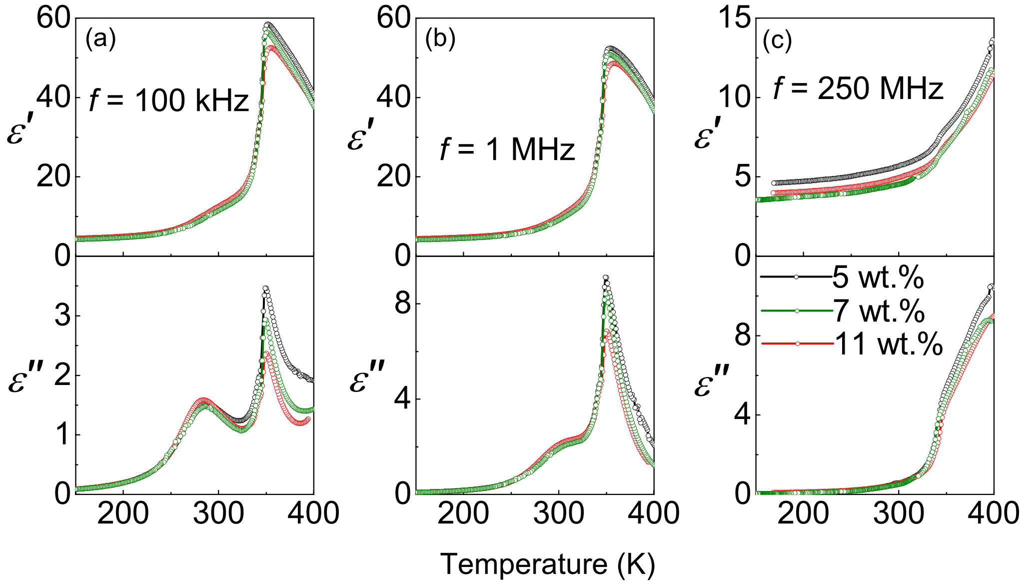

Fig. 2. Temperature dependence of the complex dielectric permittivity of nanocomposites at (a) 100 kHz, (b) 1 MHz and (c) 250 MHz.

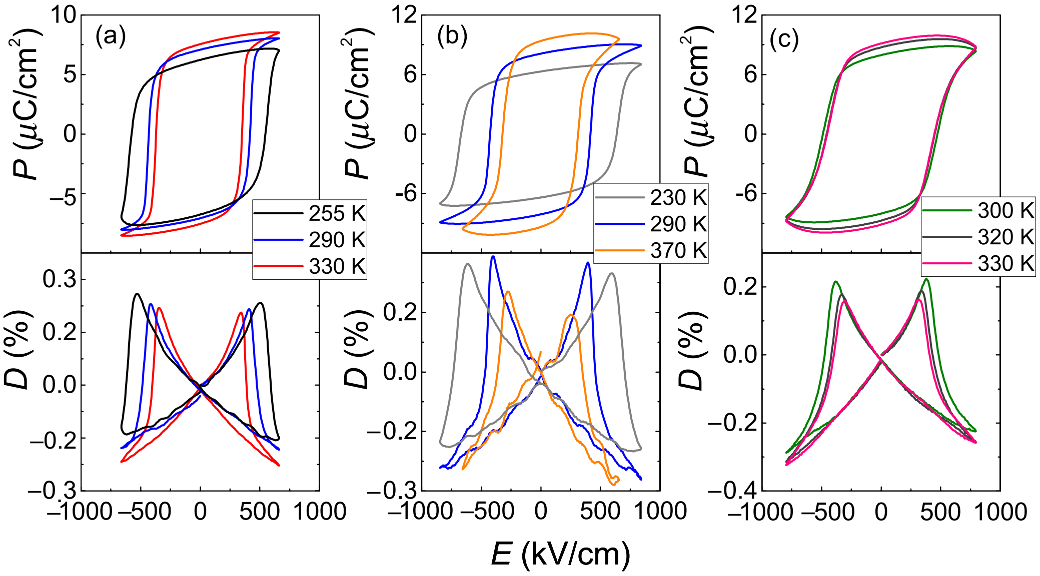

Fig. 3. Temperature effect on the electric field-polarization (E-P) hysteresis loops and electric field-displacement (E-D) hysteresis loops for the composites with $CoFe_2O_4$ content of (a) 5 wt.%, (b) 7 wt.% and (c) 11 wt.%.

the composite. The E-P loops indicate the change of polarization with an applied electric field as the chains in the crystal lamellae undergo rotation and are, therefore, closely related to electromechanical performance [25].

Figure 3 reveals that the saturation polarization increases with increasing filler content in the matrix. This enhancement in the maximum polarization value of polymer/ferrite nanocomposites can be explained by two theories: on the one hand, ferrite $CoFe_2O_4$ nanofillers may introduce additional free charges required to compensate and stabilize the polarization domain. If the free charges are present in the composite, hysteresis loops are modified. This is observed for the 11 wt.% composite – the switching exists in the composite but it is not as ideal as loops with lower concentration of ferrites (i.e. the loops have a round top and bottom which indicates the contribution of conductivity or charge separation). The tilting of the ferroelectric loops in 11 wt.% composites can be related to an inhomogeneuos distribution of fillers in the polymer matrix and resulting scattering of the electric field. On the other hand, ferrites can act as heterogeneous nucleation centres for ferroelectric domains during the polarization process [26]. Furthermore, large interfacial areas in the composites containing nanoscale fillers stimulate the exchange coupling effect through a dipolar interface layer and this results in higher polarization states and dielectric responses [15]. Additionally, Fig. 3 reveals that as temperature increases, the hysteresis loops become narrower and the polarization saturates at lower voltages, corresponding to a decrease in coercive field. Unfortunately, the increase of coercive field is observed when the concentration of inclusions is increased (Fig. 4(a)). Usually, the addition of inclusions to the PVDF matrix is performed in order to lower the coercive field of the material. This was successfully performed with the inclusions of PZT based nanoparticles to PVDF–TrFE [27].

An excellent switching behaviour was obtained for the 5 and 7 wt.% samples. This can be observed at higher temperatures. It is important to note that at lower temperatures we did not have sufficient voltage to get the full hysteresis (usually to observe the full hysteresis you need fields 1.5 times larger than the coercive field), although the peak in the current vs field graph is still observed. This fact leads to a slightly false temperature dependence of remanent polarization (Fig. 4(c)).

In addition to the E-P field hysteresis loop, the polarization switching by electric field in ferroelectric materials leads to the electric field-displacement (E-D) hysteresis, as shown in Fig. 3.

Such E-D hysteresis loop, also known as a butterfly loop, is due to three types of effects. One is

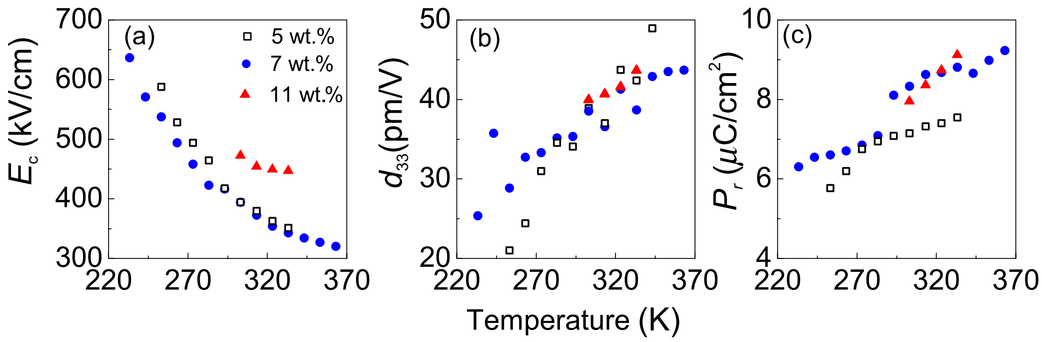

Fig. 4. Temperature effect on (a) coercive field; (b) piezoelectric response (d_{33}) and (c) remanent polarization.

the normal converse piezoelectric effect of the lattice, and the other two are due to switching and movement of walls between the zones with homogeneous polarization [26].

The coercive field exhibits a decrease with increasing temperature as expected by the Landau–Ginzburg (LG) phenomenology of the first-order phase transitions [28]. Finally, the piezoelectric response of the multiferroic composites increases with temperature due to the increased mobility of the molecular dipoles in the polymer [29, 30]. It is worth noting that the piezoelectric behaviour is similar in all the composites. Temperature dependence of a large signal d_{33} coeficient ascertains this fact.

4. Conclusions

$CoFe_2O_4$/PVDF magnetoelectric nanocomposites have been prepared, with $CoFe_2O_4$ contents ranging from 5 to 11 wt.%, by solvent casting. Aiming to meet practical application needs, the influence of temperature, frequency and ferrite content on the dielectric, ferroelectric and piezoelectric responses of magnetoelectric $CoFe_2O_4$ nanocomposites has been studied.

No substantial differences were observed on the ε' and ε'' values for frequencies lower than 100 kHz. For higher frequencies (100 kHz – 250 MHz) and at temperatures ranging from 150 to 400 K a different trend was observed, the ε' and ε'' values are higher on the composite with 5 wt.% of ferrite content and lower in the composites with 11 wt.%, indicating that for those high frequencies the $CoFe_2O_4$ nanoparticles decrease the dielectric response of the composites.

For all compositions increasing temperature leads to lower coercive fields and higher piezoelectric and polarization values reaching excellent values for applications at temperatures up to 370 K.

Acknowledgements

The authors thank FEDER funds through the COMPETE 2020 Programme and National Funds through FCT – Portuguese Foundation for Science and Technology under Strategic Funding UID/FIS/04650/2013 and projects PTDC/EEI-SII/5582/2014 and PTDC/CTM-ENE/5387/2014. P. Martins thanks the FCT – Fundação para a Ciência e Tecnologia for the financial support under Grant SFRH/BPD/96227/2013. SLM thanks for the financial support from the Basque Government Industry Department under the ELKARTEK Program.

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DIELEKTRINIO IR PJEZOELEKTRINIO ATSAKO TEMPERATŪRINĖS IR DAŽNINĖS PRIKLAUSOMYBĖS MAGNETOELEKTRINIUOSE P(VDF-TrFE)/$CoFe_2O_4$ KOMPOZITUOSE

Š. Svirskas [a], J. Belovickis [a], D. Šemeliovas [a], P. Martins [b], S. Lanceros-Méndez [b, c, d], J. Banys [a]

[a] *Vilniaus universiteto Fizikos fakultetas, Vilnius, Lietuva*
[b] *Minho universitetas, Braga, Portugalija*
[c] *Biskajos mokslų ir technologijų parkas, Derio, Ispanija*
[d] *Ikerbasque – Baskų mokslo fondas, Bilbao, Ispanija*

Santrauka

Polivinilideno fluorido-trifluoroetileno (PVDF-TrFE) kopolimerai, palyginti su kitais polimerais, pasižymi geriausiomis pjezoelektrinėmis savybėmis. Darbe tirinėjamas kompozitų, pagamintų PVDF-TrFE ir kobalto ferito pagrindu, dielektrinis ir pjezoelektrinis atsakas. Dviejų fazių multiferoikai – perspektyvios medžiagos, tačiau feroelektrinės ir magnetinės fazių funkcionalumą tokiose medžiagose realizuoti labai sunku. Visų pirma įtakos turi šių kompozitų homogeniškumas, sandūrų tarp skirtingų fazių savybės. Dėl šios priežasties būtina tyrinėti elektrinį ir elektromechaninį tokių inovatyvių kompozitų atsaką. Tyrimai leidžia nustatyti užpildo įtaką polimero matricai.

Dielektriniai tyrimai atskleidė, kad dalelės pasiskirsčiusios polimerinėje matricoje homogeniškai, nepastebėta parazitinių relaksacijų dėl nekokybiškų sandūrų tarp ferito ir polimero. Pjezoatsakas ir feroelektrinės histerezės yra palyginamos su grynuoju PVDF-TrFE polimeru. Tai reiškia, kad dėl papildomų atsiradusių sandūrų polimero savybės nedegraduoja, elektrinės ir pjezoelektrinės savybės išlieka nepakitusios. Šis rezultatas labai svarbus tolimesnei dvifazių multiferoikų raidai.