FUNCTIONAL PROPERTIES OF PVDF-BASED NZF-BT FLEXIBLE FILMS

R. Grigalaitis [a], R. Šalaševičius [a], J. Banys [a], M. Vijatovic Petrovic [b], A. Dzunuzovic [b],

M.A. Zaghete [c], G.F. Teixeira [c], and B. Stojanovic [b]

[a] *Faculty of Physics, Vilnius University, Saulėtekio 9, 10222 Vilnius, Lithuania*
[b] *Institute for Multidisciplinary Research, University of Belgrade, Belgrade, Serbia*
[c] *Institute of Chemistry, São Paulo State University (Unesp), Araraquara, Brazil*
Email: robertas.grigalaitis@ff.vu.lt

Flexible multiferroic composite films are perspective materials for sensors, actuators and similar components of wearable and stretchable devices. Here we present the study of functional properties of flexible composites prepared by embedding nickel zinc ferrite and barium titanate powder into polyvinylidene fluoride (PVDF) polymer optimizing the ratio of polymer and fillers to get the best flexibility and functionality. ATR-FTIR analysis revealed that hot pressing of the flexible films caused a transformation of about 38% of the electro-inactive PVDF α phase into electrically active β and γ phases. Broadband dielectric spectroscopy revealed two relaxation processes responsible for PVDF and space charge relaxations. Activation energies of both processes and the freezing temperature of PVDF to the glass phase were estimated for all films. Ferroelectric measurements have shown unsaturated hysteresis loops for all samples, although the clear dependence of the amount of the electrically active phase on polarization values of composites is visible.

Keywords: composites, flexible films, ferroelectric properties, dielectric dispersion

1. Introduction

Flexible ceramic-polymer composites are becoming a topic of interest for both academy and industry due to the possibility to combine mechanical flexibility with the remarkable electrical and/or magnetic properties such as high dielectric permittivity, good magnetic and piezoelectric properties [1]. Coupling of ferroelectric and ferromagnetic phenomena would be attractive for multifunctional devices, thus flexible devices are promising components for wearable and stretchable electronics – especially for medical purposes, energy harvesting and conversion, sensors, etc. [2–4].

Polyvinylidene fluoride (PVDF) is one of the frequently used electroactive polymer for this purpose due to its excellent flexibility, chemical resistance and tunability. Flexible PVDF-based composite materials can be prepared by different methods, such as solvent casting, electrospinning and hot pressing [5, 6]. The latter method has the advantage being solvent-free and cost-effective. PVDF is a semicrystalline polymer material well known for its piezoelectric, pyroelectric and ferroelectric properties [7]. Depending on the crystallization conditions it can be transformed into the one of five crystalline phases (α, β, γ, δ and ε), of which β and γ are the most interesting since they possess spontaneous polarization [8, 9].

Since the dielectric permittivity of PVDF is quite low, by loading it with ferroelectric fillers a composite material can be prepared with an increased dielectric permittivity. On the other hand, inclusion of ferrites in the PVDF might add

a ferromagnetic state to such a composite. Advances in material manufacturing during last decades have allowed one to create composite materials where both ferroelectric and ferromagnetic phases coexist together and even can be indirectly coupled through ferroelasticity and magnetostriction, respectively [10]. Often in such composites $BaTiO_3$ (barium titanate, BT) or $PbZr_xTi_{1-x}O_3$ (lead zirconium titanate, PZT) based materials are used as a ferroelectric counterpart while the magnetic phase is induced by $CoFe_2O_4$ (cobalt ferrite, CF), $NiFe_2O_4$ (nickel ferrite, NF) or $Ni_xZn_{1-x}Fe_2O_4$ (nickel zinc ferrite, NZF) spinels. Numerous investigations of functional properties of di-phase composites have been done by us [11–15] and other scientists [16–18], but flexible composites are only gaining attention from scientific community [19–22]. The main purpose of this work is to investigate the microstructural, dielectric and ferroelectric properties of flexible films prepared from PVDF with ferroelectric BT and magnetic NZF inclusions. We believe this data will be useful for further improvement of functional properties of flexible multiferroic composites and may lead to their applications in bendable devices.

2. Experiment

BT and NZF powders were prepared by the auto-combustion method as described in Ref. [23] and they were further used for the preparation of composites by their mixing in different mass ratios. These composites were embedded into a PVDF matrix by the hot pressing method under the defined and optimized pressure and temperature. The thickness of the prepared flexible films was around 50 microns. Three flexible composite films differing by NZF and BT mass ratio (indicated by numbers in parenthesis) were prepared and employed for further analysis: NZF-BT(90-10)/PVDF, NZF-BT(50-50)/PVDF and NZF-BT(10-90)/PVDF. The volume ratio between the ceramic filler and the polymer matrix was 30 to 70 vol% in the flexible composite in order to have the maximum possible flexibility of the films and not to sacrifice their functional properties.

The flexible films were analyzed by Fourier transform infrared spectroscopy (FTIR), which is a useful technique to identify the crystalline phases of the PVDF matrix. It is highly important for the estimation of the electroactive phases (β and/or γ) amount of this polymer in each composite. The analyses were carried out in the attenuated total reflectance (ATR) mode by using a *Perkin-Elmer* Spectrum Two™ FTIR spectrometer and the spectra were collected in the 4000–400 cm⁻¹ wavenumber range. Equation (1) was used to estimate the relative fraction of the electroactive phase(s) F_{EA} on the normalized spectra, subtracted from the contribution of the filler [8, 9, 24]

$$F_{EA} = \frac{I_{EA}}{1.26 I_\alpha + I_{EA}} \cdot 100, \qquad (1)$$

where I_{EA} is the absorbance of the band at about 840 cm⁻¹ that can be assigned to the β and/or γ phase, I_α is the absorbance of a characteristic band of the α phase and 1.26 is the ratio between the absorption coefficients at the respective wavenumbers. As suggested by Cai et al. [25], when β and γ phases were present simultaneously, the peak-to-valley height ratio between the two peaks around 1275 and 1234 cm⁻¹ was used to separate the two contributions F_β and F_γ.

To prepare samples for electrical measurements, silver contacts in the form of disks (3 mm in diameter) were applied on the both surfaces of flexible films. The dielectric properties of all flexible composites were measured in the cooling regime from 420 down to 120 K temperatures by employing an LCR meter (HP4284A, *Hewllet-Packard*) in the frequency range from 100 Hz to 1 MHz and a vector network analyzer (Agilent 8714ET) from 1 to 100 MHz. Complex dielectric permittivity was calculated using a flat capacitor approach from the measured capacity and tanδ values at frequencies up to 1 MHz. At higher frequencies, a complex reflection coefficient was measured of the short-circuited coaxial line with the sample placed at its end and the dielectric permittivity was calculated from the reflection magnitude and phase values. For precise temperature monitoring a *Keithley* Integra 2700 multimeter, equipped with either a *T* type thermocouple or a 100 Ω platinum resistor, was used.

Ferroelectric measurements were carried out on a precision multiferroic test system equipped with a high voltage interface (*Radiant Technologies, Inc.*) applying an alternating electric field up to 330 kV/cm at 1 Hz frequency.

3. Results and discussion

3.1. FTIR spectroscopy

The ATR-FTIR analysis (Fig. 1) of the PVDF powders has shown a predominance of the α phase, where the principal peaks characteristic of this non-polar polymorph at 1423, 1383, 1209, 1149, 975, 854, 795, 763, 614, 532, 489 and 410 cm^{-1} are clearly visible. The hot-pressing processing of the polymer induces the formation of electroactive PVDF phases, indicated by the peak around 840 cm^{-1} in the spectrum. The presence of the band at 1234 cm^{-1} can be ascribed exclusively to the γ phase and at 1275 cm^{-1} to the β phase, and this suggests that both the polar polymorphs are simultaneously present in the flexible polymer films.

The broad band at around 503 and 546 cm^{-1}, the intensity of which increases by increasing the filler amount, is due to the BT and NZF powders, respectively, and it is connected to the metal–oxygen (M-O) stretching vibrations. In all the composites the peaks characteristic of the two electroactive phases (i.e. β and γ) are identifiable but with a different intensity depending on the film composition. Using Eq. (1) the amounts of α (F_α) and electroactive phases, β (F_β) and γ (F_γ), were derived. The amount of electrically inactive α phase is dominant and the electroactive phases in all flexible films NZF-BT/PVDF/ possessed 37–40% of the most desirable ferroelectric β phase with traces of the γ phase [8, 9, 24–27]. This

percentage slightly increased with the amount of NZF in the film. For the comparison, flexible films prepared from pure BT and NZF powders have shown the formation of the same amount of the electroactive β phase, ~38%.

3.2. Dielectric properties

The temperature evolution of the complex dielectric permittivity for all measured films is presented in Fig. 2. Two overlapped peaks can be distinguished in the real part of the complex dielectric permittivity data of all compositions above 200 K. At lower temperatures, the dielectric dispersion tends to decrease to a value less than 10 and dielectric losses go to zero for all the composite films measured, in agreement to previous investigations of PVDF-based composites [22, 28–30].

The broad dielectric dispersion, visible above 200 K as a steep increase with a subsequent saturation in the real part and a corresponding peak in the imaginary part of dielectric permittivity, can be attributed to the relaxation of electroactive β and γ phases, since it is visible not only in PVDF-based composites, but in the pure PVDF as well [31]. This relaxation slows down on cooling with a following freezing to the glassy state below the room temperature.

Another dispersion region, clearly visible as a peak in both real and imaginary parts of the dielectric permittivity above 350 K, extends till the highest temperatures reached in our experiments (~420 K).
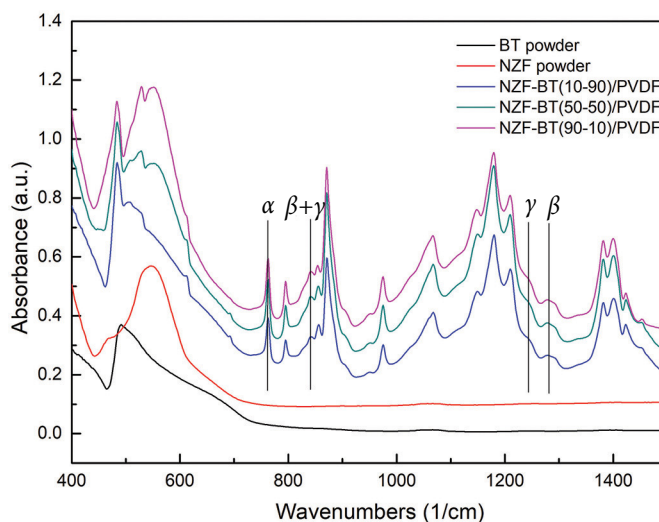

Fig. 1. FTIR ATR mode for all investigated flexible films and BT and NZF powders.
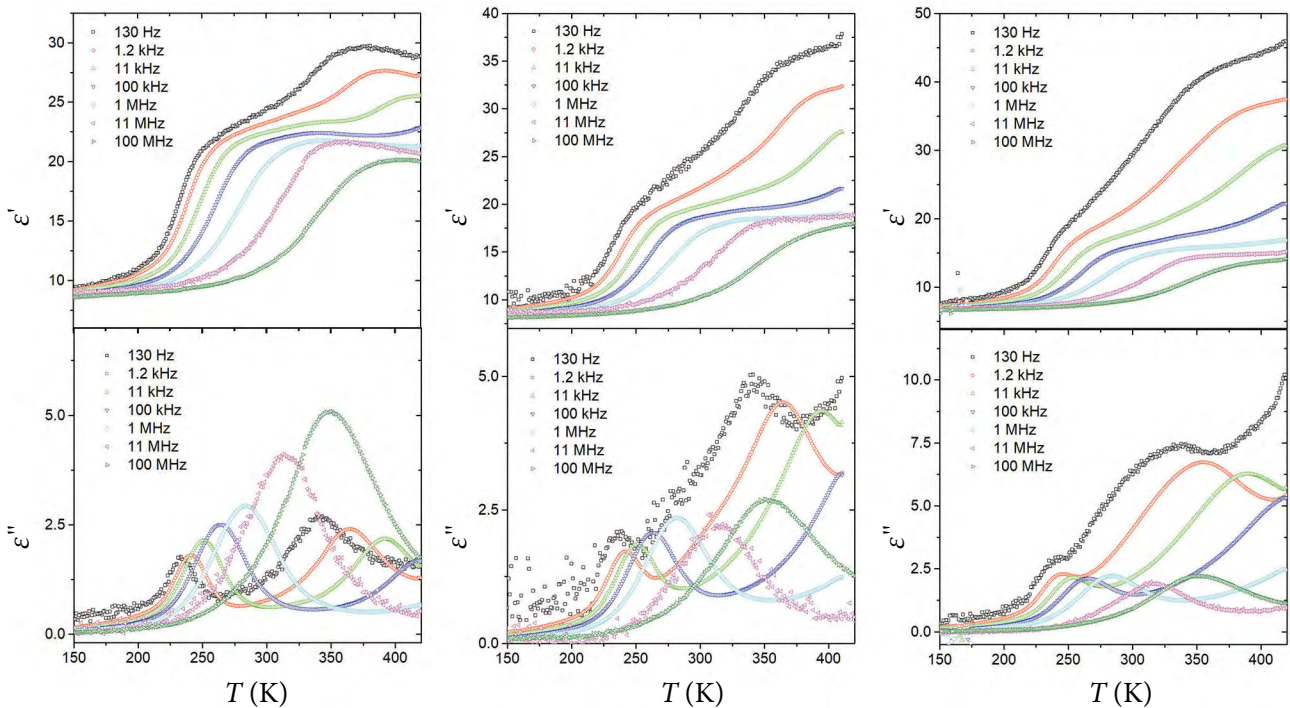
Fig. 2. Temperature dependences of dielectric permittivity of NZF-BT(10-90)/PVDF (left), NZF-BT(50–50)/PVDF (middle) and NZF-BT(90-10)/PVDF (right) flexible films at several selected frequencies.

It significantly overlaps with the PVDF-based relaxation around the room temperature at low frequencies and moves toward higher temperatures on the increase of the measurement frequency, disappearing completely from the temperature window above 1 MHz. It is interesting to note that this dispersion strength increases with the BT concentration in the composite. Since it appears in PVDF-based materials only by doping with ferromagnetic and/or ferroelectric phases, as confirmed in previous works [22], we can attribute this process to the relaxation of charge carriers accumulated at the interfaces between different phases – usually called a Maxwell–Wagner relaxation.

To obtain more information about relaxation processes in these flexible films we analyzed the data in the frequency domain. Figure 3(a) shows the frequency dependences of the complex dielectric permittivity of NZF-BT(50-50)/PVDF film. At high temperatures, close to the melting point of PVDF, two partially overlapped dispersion regions can be easily distinguished. One of them is located mainly at microwaves, another one below MHz frequencies. On cooling both relaxations move toward lower frequencies, thus, the low frequency process disappears from our frequency window

below 350 K. Since the dielectric dispersion of all composites looks qualitatively similar, we present the comparison of dielectric dispersions at different temperatures in Fig. 3(b). One can easily deduce that adding more BT to the composite increases its dielectric permittivity at microwaves, while below kHz frequencies, where the low frequency process starts dominating in dielectric dispersion, we see the opposite behaviour. Barium titanate is the well-known ferroelectric material with a high value of dielectric permittivity even at room temperature, so the increase in the dielectric response of composite films adding more BT is the expected result. On the other hand, adding more NZF obviously creates more interfaces between ferroelectrically and ferromagnetically active phases, thus leading to the formation of localized charge accumulation at these interfaces. This leads to space charge polarization, usually called in the literature as Maxwell–Wagner relaxation, that increases both dielectric losses as well as the real part of the dielectric permittivity at low frequencies.

To gain more information from the dispersion, we analyzed the data within the Cole–Cole formalism with the added conductivity term to take into account the increase of dielectric losses at low frequencies and high temperatures:
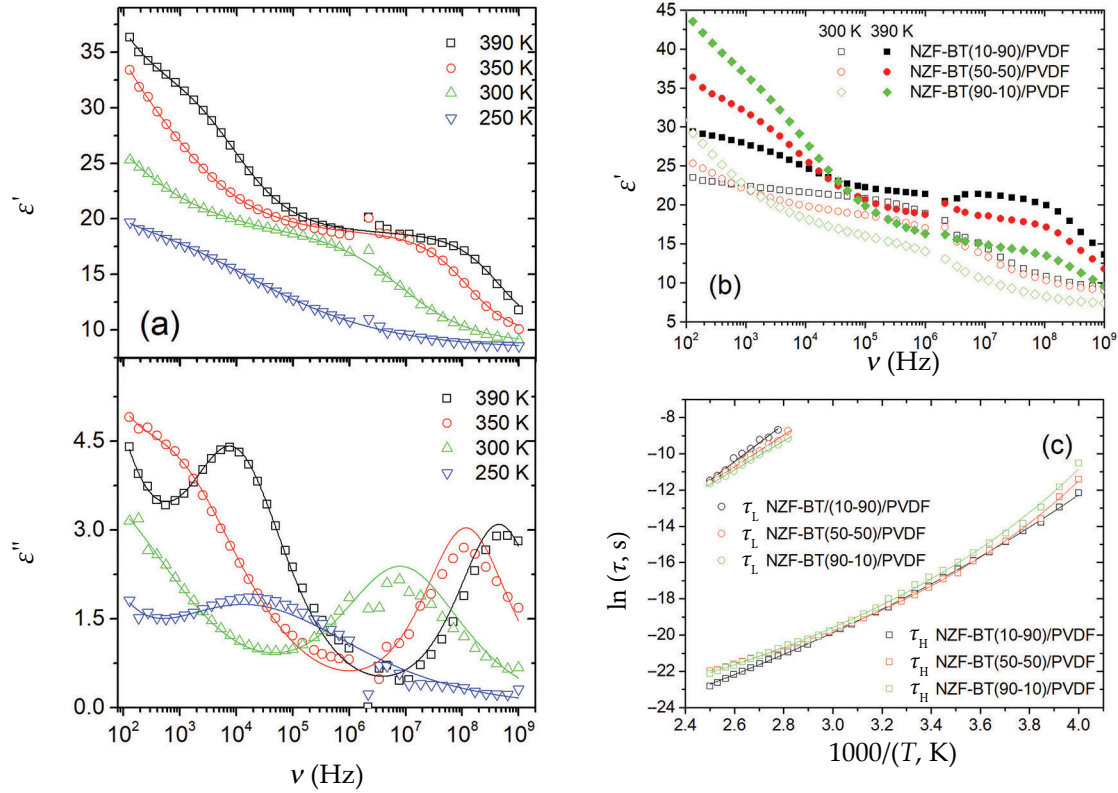
Fig. 3. Frequency dependences of dielectric properties of the NZF-BT(50-50)/PVDF flexible films at several selected temperatures (a), where symbols represent the measured data points and lines show the fits by Eg. (2); the comparison of ε' frequency dependences of all flexible films at room and 390 K temperatures (b) and the inverse temperature dependences of their characteristic relaxation times (c) obtained from the Cole–Cole fits described by Arrhenius or Vogel-Fulcher relationships (solid lines).

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_H}{1+(i\omega\tau_H)^{1-\alpha_H}}$$

$$+\frac{\Delta\varepsilon_L}{1+(i\omega\tau_L)^{1-\alpha_L}} + i\frac{\sigma}{\varepsilon_{0\omega}}. \tag{2}$$

Here the parameter ε_∞ includes the contribution of electronic polarization and atomic vibrations to the dielectric permittivity, parameters $\Delta\varepsilon$, α and τ are the dielectric strength, distribution width and the mean relaxation time of high and low frequency processes, denoted in the formula by subscripts H and L, respectively. σ is the electrical conductivity of the sample, ω is the angular frequency, and ε_0 is the permittivity of the free space.

The temperature dependence of the mean relaxation times τ_L and τ_H are presented in Fig. 3(c). It is easy to notice that τ_L values for all investigated films follow the thermally activated behaviour and can be described by the Arrhenius relationship $\tau \sim \exp(E_a/T)$ fairly well. The calculated activation energies E_a are around 0.7 eV for all

specimens and are well below 1 eV, which is considered as the activation energy related to oxygen vacancies [32], thus confirming our assumption about space charge polarization related phenomena. The mean relaxation time of high-frequency relaxation, τ_H, shows a nonlinear dependence in the respect of the inverse temperature and was fitted with the Vogel–Fulcher relationship:

$$\tau = \tau_0 \exp\left(\frac{E_a}{T-T_f}\right). \tag{3}$$

Here τ_0 is the relaxation time at infinite temperature, E_a is the activation energy of dipoles, and T_f is their their freezing temperature. The obtained values of fits are presented in Table 1.

Usually, the divergence of the mean relaxation time means the transition of the material to a glass state. It was proven experimentally that such a transition occurs in pure PVDF as well as in PZT-PVDF composites [29]. So, the high frequency

Table 1. Comparison of the fitting parameters of the mean relaxation time τ_H for all flexible films.

	τ_0, s	E_a, eV	T_f, K
NZF-BT(10-90)/PVDF	$1.4\pm0.35\times10^{-14}$	0.22 ± 0.008	118 ± 3.4
NZF-BT(50-50)/PVDF	$1.4\pm0.21\times10^{-12}$	0.1 ± 0.003	174 ± 1.9
NZF-BT(90-10)/PVDF	$5.2\pm1.4\times10^{-13}$	0.12 ± 0.006	167 ± 3.2

dipolar dynamics can be related to the relaxation of dipoles formed by electroactive PVDF phases. For NZF-BT(50-50)/PVDF and NZF-BT(90-10)/ PVDF films we obtained similar values of activation energies in comparison to the abovementioned PZT-PVDF composite, but freezing temperatures are significantly lower. This is not surprising, since freezing temperatures can be significantly reduced depending on the size, type and distribution of particles dispersed in PVDF. A somewhat unexpected result was nearly twice higher value of the activation energy and, respectively, a lower value of the freezing temperature for the NZF-BT(10-90)/ PVDF sample, but this, again, can be related to a slightly different distribution of the ferroelectric and ferromagnetic phases within PVDF.

3.3. Ferroelectric properties

There is a lot of factors that can influence the ferroelectric properties of films – such as interface areas, agglomerations, voids, an inhomogeneous distribution of filler in the polymer matrix, etc. [19, 26]. Among them all, a couple of effects are most influential and have to be considered. The first one is the concentration of barium titanate as a ferroelectric phase in the flexible polymer film. The results of the room temperature polarization vs electric field measurements (presented in Fig. 4) have shown exactly the influence of the barium titanate amount on the ferroelectric properties of the films. Flexible films have shown different breakdown fields, namely, for NZF-BT(90-10)/PVDF it was 170 kVcm^{-1}, for NZF-BT(50-50)/PVDF it was 220 kVcm^{-1} and the sample NZF-BT(10-90)/PVDF managed the whole range of applied electric fields.

Non-saturated ferroelectric loops were obtained for all investigated flexible films. As expected, due to a high conductivity of ferrite phases and the presence of interfacial polarization, the sample with the largest amount of the ferrite phase has shown very lossy ferroelectric curves quite different from the conventional ferroelectric materials. The sample with the largest amount of the ferroelectric phase obviously has the potential to have more saturated ferroelectric loops and higher values of saturation polarization. However, to prove this statement, measurements at larger fields will be needed. The next effect that should be considered is the amount of the electroactive PVDF phase in the flexible films. The literature data about ferroelectric properties of pure α, β and γ PVDF
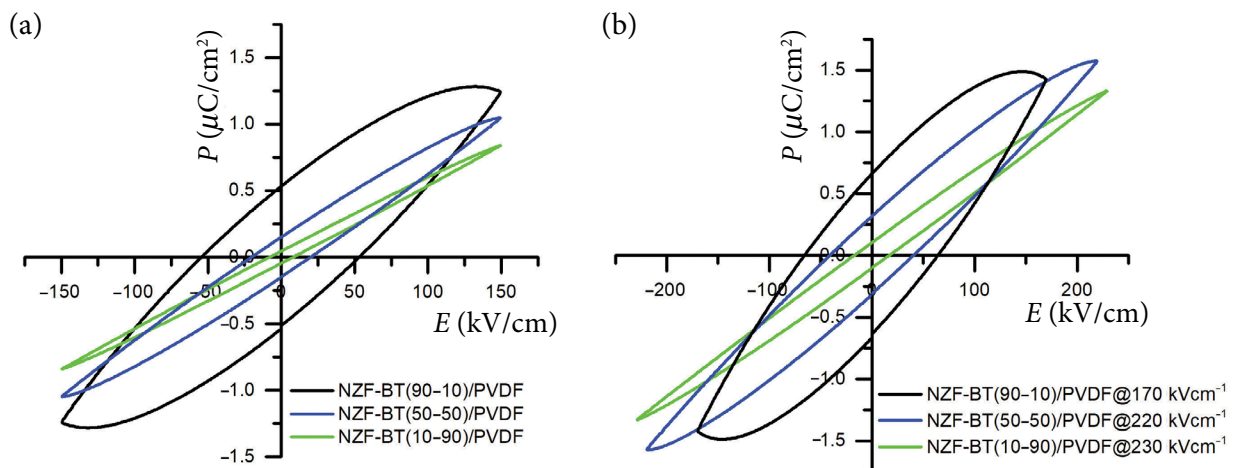

Fig. 4. Hysteresis *P–E* loops for NZF-BT(90-10)/PVDF, NZF-BT(10-90)/PVDF and NZF-BT(10-90)/ PVDF at 150 kVcm^{-1} (a) and at the max field without breakdown of the sample (b).

films suggested that there is a clear possibility that the formed type of the PVDF phase can have some effect on the ferroelectric properties of these composites as well [9, 33]. Pure β-phase PVDF shows a typical characteristic of normal ferroelectric in the rectangle-shaped loops. α and γ PVDF phases have a smaller remnant polarization under the same conditions, and P_r of γ-PVDF is slightly higher than that of α-PVDF [33]. In this case, the calculated value of electroactive PVDF phases obtained from the FT-IR analysis in all investigated films is almost the same and around 38%. Thus, we can come to the conclusion that the amount of ferroelectric/barium titanate phase in the sample has the dominant effect on the ferroelectric properties of the films. More detailed analysis should be performed in order to get clear conclusions and this will be the subject of future investigations.

4. Conclusions

In summary, we have successfully prepared the composite multiferroic films by varying the composition of ferroelectric and ferromagnetic fillers in PVDF. The hot pressing applied during the preparation of films created 38% of ferroelectrically active β and γ phases in the PVDF component of the composite.

All compositions have shown qualitatively the same dielectric behaviour that consists of PVDF-based high frequency relaxation and a space charge relaxation visible at high temperatures and low frequencies only.

We successfully observed the divergence of the mean relaxation time according to the Vogel–Fulcher law, which means the transformation of the PVDF to the glassy state. The calculated freezing temperatures are lower than in pure PVDF, but this is a usual behaviour in composite systems.

Measured ferroelectric hysteresis loops have shown no saturation for all flexible films. This result is not surprising, since the vast majority of multiferroic composites exhibit space charge accumulation at interfaces between different phases, leading to the decrease of their resistivity, especially at low frequencies. Despite that, the change of the remnant polarization value with the increase of BT content evidently shows the dominating effect on the polarization of flexible films compared to the influence of the electroactive β and γ phases of PVDF.

The increase of BT composition in all flexible films leads to the increase of the dielectric permittivity at microwaves in all the investigated temperature region. This result offers the possibility to effectively tune the value of the dielectric permittivity in these composites, which can be beneficial for applications in the field of stretchable devices.

Acknowledgements

References

[1] M. Arbatti, X. Shan, and Z.-Y. Cheng, Ceramic–polymer composites with high dielectric constant, Adv. Mater. **19**, 1369–1372 (2007), https://doi.org/10.1002/adma.200601996

[2] Y. Chu, J. Zhong, H. Liu, Y. Ma, N. Liu, Y. Song, J. Liang, Z. Shao, Y. Sun, Y. Dong, X. Wang, and L. Lin, Human pulse diagnosis for medical assessments using a wearable piezoelectret sensing system, Adv. Funct. Mater. **28**, 1803413 (2018), https://doi.org/10.1002/adfm.201803413

[3] A. Chortos and Z. Bao, Skin-inspired electronic devices, Mater. Today **17**, 321–331 (2014), https://doi.org/10.1016/j.mattod.2014.05.006

[4] J. Luo, W. Gao, and Z.L. Wang, The triboelectric nanogenerator as an innovative technology toward intelligent sports, Adv. Mater. **33**, 2004178 (2021), https://doi.org/10.1002/adma.202004178

[5] D. Lolla, M. Lolla, A. Abutaleb, H. Shin, D. Reneker, and G. Chase, Fabrication, polarization of electrospun polyvinylidene fluoride electret fibers and effect on capturing nanoscale solid aerosols, Materials **9**, 671 (2016), https://doi.org/10.3390/ma9080671

[6] A. Seema, K.R. Dayas, and J.M. Varghese, PVDF-PZT-5H composites prepared by hot press and tape casting techniques, J. Appl. Polym. Sci. **106**, 146–151 (2007), https://doi.org/10.1002/app.26673

[7] C. Wisniewski, G.F.L. Ferreira, W.A. Moura, J.A. Giacometti, C. Wisniewski, and G.F.L. Ferreira, Study of ferroelectric polarization in poly(vinylidene fluoride) using the constant current method, J. Phys. D Appl. Phys. **33**, 2483–2488 (2000), https://doi.org/10.1088/0022-3727/33/19/319

[8] P. Martins, A.C. Lopes, and S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications, Prog. Polym. Sci. **39**, 683–706 (2014), https://doi.org/10.1016/j.progpolymsci.2013.07.006

[9] H.-J. Ye, L. Yang, W.-Z. Shao, S.-B. Sun, and L. Zhen, Effect of electroactive phase transformation on electron structure and dielectric properties of uniaxial stretching poly(vinylidene fluoride) films, RSC Adv. **3**, 23730 (2013), https://doi.org/10.1039/c3ra43966f

[10] C.-W. Nan, M.I. Bichurin, S. Dong, D. Viehland, and G. Srinivasan, Multiferroic magnetoelectric composites: Historical perspective, status, and future directions, J. Appl. Phys. **103**, 031101 (2008), https://doi.org/10.1063/1.2836410

[11] R. Grigalaitis, M.M. Vijatović Petrović, D. Baltrūnas, K. Mažeika, B.D. Stojanović, and J. Banys, Broadband dielectric and Mössbauer studies of $BaTiO_3$–$NiFe_2O_4$ composite multiferroics, J. Mater. Sci.: Mater. Electron. **26** (2015), https://doi.org/10.1007/s10854-015-3641-8

[12] A.S. Dzunuzovic, M.M. Vijatovic Petrovic, J.D. Bobic, N.I. Ilic, M. Ivanov, R. Grigalaitis, J. Banys, and B.D. Stojanovic, Magneto-electric properties of $xNi_{0.7}Zn_{0.3}Fe_2O_4$ – $(1-x)BaTiO_3$ multiferroic composites, Ceram. Int. **44**, 683–694 (2018), https://doi.org/10.1016/j.ceramint.2017.09.229

[13] A. Sakanas, D. Nuzhnyy, R. Grigalaitis, J. Banys, F. Borodavka, S. Kamba, C.E. Ciomaga, and L. Mitoseriu, Dielectric and phonon spectroscopy of Nb-doped $Pb(Zr_{1-y}Ti_y)O_3$-$CoFe_2O_4$ composites, J. Appl. Phys. **121** (2017), https://doi.org/10.1063/1.4984199

[14] A. Sakanas, R. Grigalaitis, J. Banys, L. Curecheriu, L. Mitoseriu, and V. Buscaglia, Microstructural influence on the broadband dielectric properties of $BaTiO_3$-$Ni_{0.5}Zn_{0.5}Fe_2O_4$ core-shell composites:

Experiment and modeling, J. Appl. Phys. **118** (2015), https://doi.org/10.1063/1.4935138

[15] A.S. Dzunuzovic, M.M.V. Petrovic, J.D. Bobic, N.I. Ilic, and B.D. Stojanovic, Influence of ferrite phase on electrical properties of the barium zirconium titanate based multiferroic composites, J. Electroceram. **46**, 57–71 (2021), https://doi.org/10.1007/s10832-021-00244-9

[16] S. Singh, N. Kumar, R. Bhargava, M. Sahni, K. Sung, and J.H. Jung, Magnetodielectric effect in $BaTiO_3$/$ZnFe_2O_4$ core/shell nanoparticles, J. Alloys Compd. **587**, 437–441 (2014), https://doi.org/10.1016/j.jallcom.2013.10.136

[17] R.A. Mondal, B.S. Murty, and V.R.K. Murthy, Dielectric, magnetic and enhanced magneto-electric response in high energy ball milling assisted BST-NZF particulate composite, Mater. Chem. Phys. **167**, 338–346 (2015), https://doi.org/10.1016/j.matchemphys.2015.10.053

[18] D. Padmapriya, D. Dhayanithi, M.T. Rahul, N. Kalarikkal, and N.V. Giridharan, Study of room-temperature magnetoelectric coupling in $(1-x)BaTiO_3$ and $(x)NiFe_2O_4$ multiferroic composites, Appl. Phys. A **127**, 293 (2021), https://doi.org/10.1007/s00339-021-04431-x

[19] M. Vijatovic Petrovic, F. Cordero, E. Mercadelli, E. Brunengo, N. Ilic, C. Galassi, Z. Despotovic, J. Bobic, A. Dzunuzovic, P. Stagnaro, G. Canu, and F. Craciun, Flexible lead-free NBT-BT/PVDF composite films by hot pressing for low-energy harvesting and storage, J. Alloys Compd. **884**, 161071 (2021), https://doi.org/10.1016/j.jallcom.2021.161071

[20] X. Du, Z. Zhou, Z. Zhang, L. Yao, Q. Zhang, and H. Yang, Porous, multi-layered piezoelectric composites based on highly oriented PZT/PVDF electrospinning fibers for high-performance piezoelectric nanogenerators, J. Adv. Ceram. **11**, 331–344 (2022), https://doi.org/10.1007/s40145-021-0537-3

[21] N. Ilić, G.F. Teixeira, J. Bobić, V. Spasojević, A. Džunuzović, M.V. Petrović, M.Ap. Zaghete, and B. Stojanović, Auto-combustion synthesis as a method for preparing $BiFeO_3$ powders and flexible $BiFeO_3$/PVDF films with improved magnetic properties. Influence of doping ion position, size

and valence on electric properties, Mater. Sci. Eng. B **280**, 115686 (2022), https://doi.org/10.1016/j.mseb.2022.115686

[22] J.D. Bobić, G.F. Teixeira, R. Grigalaitis, S. Gyergyek, M.M.V. Petrović, M.A. Zaghete, and B.D. Stojanovic, PZT–NZF/CF ferrite flexible thick films: Structural, dielectric, ferroelectric, and magnetic characterization, J. Adv. Ceram. **8**, 545–554 (2019), https://doi.org/10.1007/s40145-019-0337-1

[23] A.S. Dzunuzovic, M.M.V. Petrovic, B.S. Stojadinovic, N.I. Ilic, J.D. Bobic, C.R. Foschini, M.A. Zaghete, and B.D. Stojanovic, Multiferroic (NiZn) Fe_2O_4–$BaTiO_3$ composites prepared from nanopowders by auto-combustion method, Ceram. Int. **41**, 13189–13200 (2015), https://doi.org/10.1016/j.ceramint.2015.07.096

[24] L. Yang, J. Qiu, K. Zhu, H. Ji, Q. Zhao, M. Shen, and S. Zeng, Effect of rolling temperature on the microstructure and electric properties of β-polyvinylidene fluoride films, J. Mater. Sci.: Mater. Electron. **29**, 15957–15965 (2018), https://doi.org/10.1007/s10854-018-9681-0

[25] X. Cai, T. Lei, D. Sun, and L. Lin, a critical analysis of the α, β and γ phases in poly(vinylidene fluoride) using FTIR, RSC Adv. **7**, 15382–15389 (2017), https://doi.org/10.1039/C7RA01267E

[26] W.J. Kim, M.H. Han, Y.-H. Shin, H. Kim, and E.K. Lee, First-principles study of the α–β phase transition of ferroelectric poly(vinylidene difluoride): observation of multiple transition pathways, J. Phys. Chem. B **120**, 3240–3249 (2016), https://doi.org/10.1021/acs.jpcb.6b00881

[27] G.T. Davis, J.E. McKinney, M.G. Broadhurst, and S.C. Roth, Electric-field-induced phase changes in poly(vinylidene fluoride), J. Appl. Phys. **49**, 4998–5002 (1978), https://doi.org/10.1063/1.324446

[28] Š. Svirskas, J. Belovickis, D. Šemeliovas, P. Martins, S. Lanceros-Méndez, and J. Banys, Temperature and frequency dependence of the dielectric and piezoelectric response of P(VDF-TrFE)/$CoFe_2O_4$ magnetoelectric composites, Lith. J. Phys. **57**(2), 103–111 (2017), https://doi.org/10.3952/physics.v57i2.3517

[29] B. Hilczer, J. Kułek, E. Markiewicz, M. Kosec, and B. Malič, Dielectric relaxation in ferroelectric PZT–PVDF nanocomposites, J. Non-Cryst. Solids **305**, 167–173 (2002), https://doi.org/10.1016/S0022-3093(02)01103-1

[30] S. Svirskas, M. Simenas, J. Banys, P. Martins, and S. Lanceros-Mendez, Dielectric relaxation and ferromagnetic resonance in magnetoelectric (Polyvinylidene-fluoride)/ferrite composites, J. Polym. Res. **22**, 141 (2015), https://doi.org/10.1007/s10965-015-0780-9

[31] T. Furukawa, Y. Tajitsu, X. Zhang, and G.E. Johnson, Dielectric relaxations in copolymers of vinylidene fluoride, Ferroelectrics **135**, 401–417 (1992), https://doi.org/10.1080/00150199208230041

[32] S. Brahma, R.N.P. Choudhary, and A.K. Thakur, AC impedance analysis of $LaLiMo_2O_8$ electroceramics, Phys. B Condens. Matter. **355**, 188–201 (2005), https://doi.org/10.1016/j.physb.2004.10.091

[33] W. Xia and Z. Zhang, PVDF-based dielectric polymers and their applications in electronic materials, IET Nanodielectrics **1**, 17–31 (2018), https://doi.org/10.1049/iet-nde.2018.0001

FUNKCINĖS LANKSČIŲ PLĖVELIŲ PVDF PAGRINDU SU NZF IR BT SAVYBĖS

R. Grigalaitis [a], R. Šalaševičius [a], J. Banys [a], M. Vijatovic Petrovic [b], A. Dzunuzovic [b], M.A. Zaghete [c], G.F. Teixeira [c], B. Stojanovic [b]

[a] *Vilniaus universiteto Fizikos fakultetas, Vilnius, Lietuva*
[b] *Belgrado universiteto Multidisciplininių tyrimų institutas, Belgradas, Serbija*
[c] *San Paulo valstybinio universiteto Chemijos institutas, Ararakvara, Brazilija*

Santrauka

Lankstūs multiferoiniai kompozitai yra perspektyvios medžiagos dėvimų bei lanksčių įrenginių jutikliams, aktuatoriams ir kitiems komponentams. Šiame darbe pristatomi lanksčių kompozitų, pagamintų įterpiant cinko ferito ir bario titanato miltelius į polivinilideno fluorido polimerą, funkcinių savybių tyrimai. Polimero ir intarpų santykis kompozite gamybos metu buvo parenkamas taip, kad būtų pasiektas maksimalus lankstumas nepakenkiant funkcionalumui. ATR-FTIR analizė atskleidė, kad karštas lanksčių plėvelių presavimas transformavo apie 38 % elektriškai neaktyvios α fazės į elektriškai aktyvias β ir γ fazes. Plačiajuostė dielektrinė spektroskopija parodė šiose medžiagose du relaksacinius procesus, sukeltus PVDF ir atitinkamai erdvinio krūvio. Buvo įvertintos abiejų procesų aktyvacijos energijos bei PVDF stiklėjimo temperatūros visoms plėvelėms. Feroelektrinių medžiagų tyrimai parodė, kad histerezės kilpos neįsisotina. Nepaisant to, matoma aiški poliarizacijos savybių priklausomybė nuo elektriškai aktyvios fazės kiekio kompozituose.