

Article

Phase Composition, Surface Morphology, and Dielectric Properties of Poly(Vinylidene Fluoride)–Cobalt Ferrite Composite Films Depending on Thickness

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Abstract: This study investigates the effect of polyvinylidene fluoride–CoFe₂O₄ (PVDF–CFO) composite film thickness on their supramolecular structure, phase composition, and dielectric properties. The composites were synthesized from PVDF with CFO nanoparticles using the Dr. Blade method to obtain film thicknesses ranging from 15 to 58 μm. The data obtained show that the thinner film (15 μm) has a higher β-phase content compared to the thicker films (58 μm), as confirmed by FTIR and Raman spectroscopy. Scanning electron microscopy (SEM) showed that increasing film thickness within the studied range leads to the development of larger spherulitic structures and increased porosity. Atomic force microscopy (AFM) analysis also showed that thicker films have higher tensile strength due to their larger cross-sectional area, while thinner films exhibit lower elasticity. A more uniform microstructure and an increased electroactive phase in thin films result in increased permittivity, which is critical for PVDF-based sensors and energy devices.

Keywords: PVDF; multiferroic nanocomposites; phase composition; supramolecular structure



Academic Editor: Mingjun Huang

Received: 19 November 2024

Revised: 26 December 2024

Accepted: 29 December 2024

Published: 31 December 2024

Citation: Vorontsov, P.A.; Salnikov, V.D.; Savin, V.V.; Vorontsov, S.A.; Omelyanchik, A.S.; Shvets, P.V.; Panina, L.V.; Ershov, P.A.; Rodionova, V.V. Phase Composition, Surface Morphology, and Dielectric Properties of Poly(Vinylidene Fluoride)–Cobalt Ferrite Composite Films Depending on Thickness. *Crystals* **2025**, *15*, 47. <https://doi.org/10.3390/cryst15010047>

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1. Introduction

Polyvinylidene fluoride (PVDF) is a widely used polymer known for its exceptional thermal stability, chemical resistance, and ferro-, pyro-, and piezoelectric properties. These characteristics make PVDF suitable for applications in various fields such as electronics, biomedicine, and others [1]. Its high dielectric constant, stable electrochemical performance, and mechanical strength also render PVDF an ideal material for developing new separators in lithium-ion batteries [2]. Furthermore, the piezoelectric properties of PVDF enable its application in the production of pressure and vibration sensors [3,4].

The unique properties of PVDF are related to its structure and phase composition. PVDF is a polymorphic semicrystalline polymer that can exist in at least four crystalline forms (α, β, γ, and δ), each of which results from a different spatial arrangement of CH₂ and CF₂ groups [5–7]. Among them, the β- and γ-phases possess the strongest piezo- and ferroelectric properties [8,9]. The phase composition of PVDF can be influenced by various processing methods, including thermal treatment, cooling rate, and the presence of nucleating agents, such as inorganic nanoparticles [10–12]. The structure of PVDF is characterized by a combination of highly crystalline and amorphous regions. The polymer

chains organize themselves into a periodic arrangement, resulting in the formation of spherulites, which are spherical entities [13].

Building on the inherent properties of PVDF, researchers have explored ways to enhance its capabilities by incorporating other materials. One notable approach is the incorporation of magnetic nanoparticles (MNPs), such as cobalt ferrite CoFe_2O_4 (CFO), as a filler. This combination results in a PVDF-based composite that exhibits both piezoelectric and magnetic properties, creating a multiferroic material [14]. Such composites have expanded the application potential of PVDF, making them suitable for use as magnetic field sensors, transducers, multistate memory devices, and filters [15].

Despite the large number of publications on PVDF and its composite films, there is a noticeable gap in the literature regarding the effect of film thickness on phase composition, surface morphology, and dielectric properties. While many studies report film thickness, its influence on these critical properties is often overlooked. Variations in quantitative phase content are often attributed to differences in deposition methods [16]. However, it is possible that the significant presence of β -phases observed in some studies is more closely related to the thickness of the composite films than to the synthesis method itself.

For example, in the study by Javier Vicente et al. [17], PVDF composite films with thicknesses ranging from 20 to 60 μm were considered. This research focused on how mechanical properties, such as flexibility and tensile strength, vary with thickness. Thicker composites tend to have higher dielectric constants, which is advantageous for capacitor and energy storage device applications. In pressure sensor applications, the thickness of PVDF composites affects their sensitivity and response time, with thinner films offering shorter response times compared to thicker films [17]. Spin coating, a technique that allows precise control of film thickness, tends to produce films with a higher content of the β -phase. In contrast, films created by the casting method predominantly form the α -phase, while the β -phase can only be increased by polarization or stretching [18].

In their work on optimizing the piezoelectric and magnetoelectric responses in $\text{CoFe}_2\text{O}_4/\text{P(VDF-TrFE)}$ nanocomposites, Martins P. et al. [19] found that the thickness of the composite had no noticeable effect on the magnetoelectric response. The samples in their study had thicknesses of approximately 25, 50, and 75 μm . However, it is important to note that Martins P. and co-authors used a polyvinylidene fluoride copolymer (PVDF-TrFE), which predominantly exists in the β -phase regardless of the thickness of the composite film, unlike our study, which focuses on PVDF. In a study by Yuan Wang et al. [20], film thickness was shown to be a critical factor affecting the performance of piezoelectric nanogenerators. Their research compared films fabricated by the spin-coating method (thickness = 6 μm) and the casting method (thickness = 97.7 μm), highlighting the significant effect of thickness on device response.

Although there are numerous publications that study PVDF-based composite films and report the thicknesses of the films produced, such works only study the physical properties of the material as a function of thickness. However, none of the scientific papers dealing with the fabrication of PVDF-based devices, sensors, and piezoelectric nanogenerators adequately address how the thickness of composite films affects the phase composition, surface morphology, and dielectric properties.

In this work, composite films with different thicknesses ranging from 15 to 58 μm were prepared by the Dr. Blade method from PVDF and cobalt ferrite nanoparticles synthesized by the hydrothermal method. All samples were found to contain electroactive β - and γ -phases. The 15 and 20 μm thick composite films were found to have higher β -phase content and dielectric constant, while the thicker films (47 and 58 μm) contained more α - and γ -phases and had lower dielectric constant values. By analyzing the supramolecular structure of samples of different thicknesses, it was found that the formation of larger

spherulites occurred in thicker films ($5.5 \pm 1.2 \mu\text{m}$ for $58 \mu\text{m}$, $2.7 \pm 0.3 \mu\text{m}$ for $15 \mu\text{m}$). The study of elasticity showed that this parameter decreases for thicknesses less than $58 \mu\text{m}$. Young's modulus decreases from 45 MPa to 29–33 MPa for thicknesses of $47 \mu\text{m}$, $20 \mu\text{m}$, and $15 \mu\text{m}$. Thus, this work shows that the thickness of PVDF-based composite films affects the formation of the supramolecular structure (spherulites and pores), phase composition, and elasticity of the samples; as the thickness of PVDF-CFO composites decreases, the elasticity decreases, the size of spherulites and pores decreases, and the content of the electroactive β -phase and the dielectric constant increases.

In this context, the present work is the first to explore the potential for controlling the microstructure and phase composition of composite films by varying their thickness. Understanding the effect of film thickness on these properties provides valuable insights for the further development of PVDF-based composites with high electroactive β -phase content.

2. Experiment Design

2.1. Materials

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98\%$; LenReactiv, St. Petersburg, Russia), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98\%$; LenReactiv, St. Petersburg, Russia), NaOH ($\geq 98\%$; LenReactiv, St. Petersburg, Russia), sodium dodecyl sulfate (SDS, $\geq 98\%$; LenReactiv, St. Petersburg, Russia), *N,N*-Dimethylformamide (DMF, $\geq 98\%$; Ekos-1, Moscow, Russia), and polyvinylidene fluoride (PVDF, m.w. 534,000; Sigma-Aldrich, Burlington, MA, USA) were used.

2.2. Nanoparticles Synthesis

Magnetic nanoparticles were prepared by the hydrothermal method described in detail elsewhere [21]. First, cobalt nitrate (4.5 mmol) and SDS (9 mmol) were dissolved in 54 mL of distilled water at 50°C using a magnetic stirrer. Iron nitrate (9 mmol) was then added and stirred until complete dissolution. Subsequently, sodium hydroxide (67.5 mmol) was dissolved in 27 mL at 50°C and added to initiate the coprecipitation reaction. The solution was then placed in a 200 mL Teflon container (40.5 vol%), which was placed in a steel autoclave. The autoclave was heated to 150°C , followed by a reaction for 10 h. The powder obtained was washed several times with water and ethanol and dried in a desiccator at 65°C .

2.3. Fabrication of PVDF-CFO Composite Films

The PVDF-CFO composite films were produced using the Dr. Blade method, also known as knife coating or blade coating (Figure 1). The thickness of the film is controlled by adjusting the gap between the blade and the substrate. In the laboratory settings, the blade moves across the substrate while the polymer solution is placed in front of the moving blade and then dragged by it [22].

To prepare the PVDF solution, 0.9 g of PVDF powder were dissolved in 4.57 mL of DMF by stirring at 45°C for 18 h. Separately, MNPs were dispersed in 1.14 mL of DMF using an ultrasonic bath for 30 min to achieve a uniform dispersion. The mass of MNPs was selected to achieve a final concentration of 10 wt.% in the composite. The resulting solutions were then mixed and stirred for an additional 2 h at 45°C until homogeneity was achieved. The solutions were then applied to the dust-free glass and spread evenly with a blade. The coated glass was subsequently placed in an oven at 65°C for 20 h to evaporate the solvent and form solid films. After drying, the films were peeled off the glass substrates and analyzed. The range of thicknesses was obtained by varying the distance between the glass and the blade (15, 25, 60, and $95 \mu\text{m}$), ranging from 15 to $58 \mu\text{m}$. It should be noted that the thicknesses of the finished composite films were smaller compared to those placed on the blade due to shrinkage during drying.

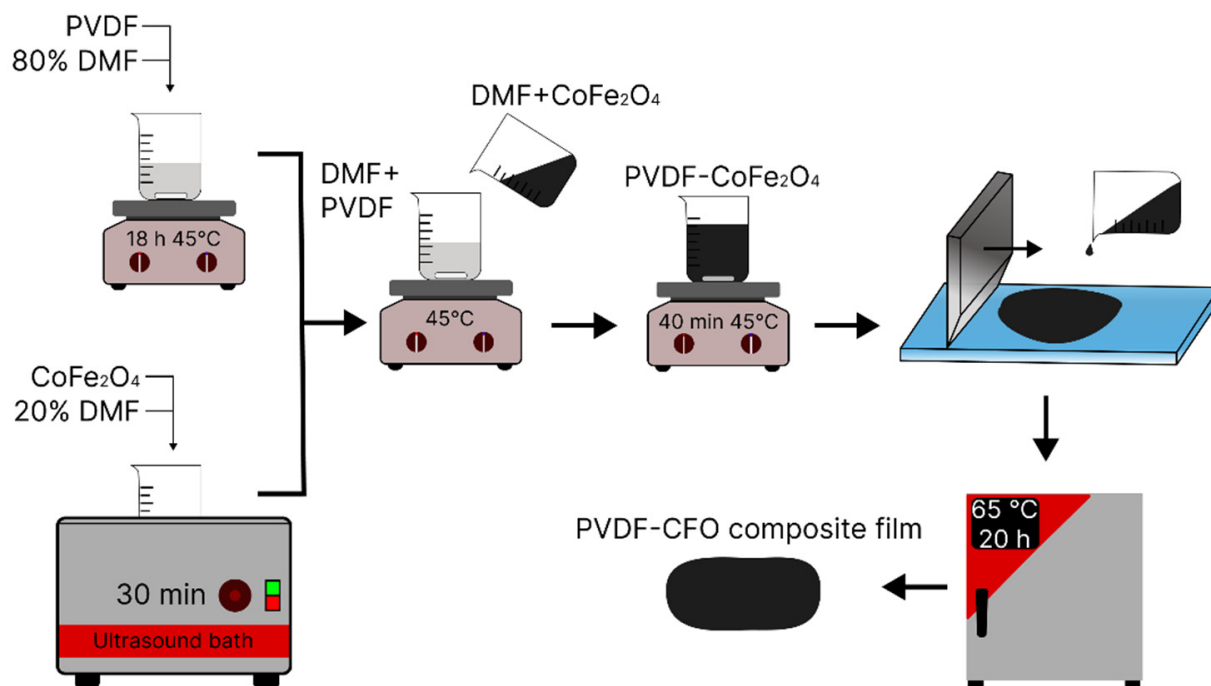


Figure 1. Schematic diagram of the fabrication process of PVDF-CFO composite films.

2.4. Characterization

Scanning electron microscopy (SEM) was used to determine the film thickness and examine the distribution of nanoparticle agglomerates, as well as the dimensions of spherulites and pores on the composite film surface. The analysis was performed using a Hitachi TM4000 Plus SEM instrument (Hitachi, Tokyo, Japan), operating in the electron backscattering mode.

After determining the thickness and size of nanoparticle spherulites, pores, and agglomerates, the surface topology studies were performed using atomic force microscopy (AFM, Ntegra, NT-MDT, Moscow, Russia). The AFM was operated in tapping (semi-contact) mode over an area of $10 \times 10 \mu\text{m}$ (512×512) using NS15 (NT-MDT, Moscow, Russia) tips. The mechanical properties of the sample surface were also evaluated using AFM in nanoindentation mode [23], in which force–distance curves were recorded at each scan point. These curves were analyzed during both collision and pullback to evaluate the morphology, surface roughness, deformation, and Young’s modulus.

To qualitatively determine the α -, β -, and γ -phase contents, the samples were analyzed using X-ray diffraction (XRD) and Raman spectroscopy. XRD analysis was performed with an AXRD Benchtop Powder X-ray Diffractometer (PROTO Mfg. Ltd., LaSalle, ON, Canada), utilizing Cu-K α radiation ($\lambda = 1.54060 \text{ \AA}$). Raman spectroscopy was performed using a Horiba Jobin Yvon micro-Raman spectrometer (LabRam HR800, France) equipped with a $\times 100$ magnification lens (numerical aperture 0.9).

The XRD scans were conducted with a step size of 0.015 degrees and a measurement time of 8 s, encompassing a 2θ range from 15° to 65° at room temperature. The determination of the average coherent scattering region was calculated via the Scherrer formula [24,25]

$$D_{XRD} = \frac{0.94 \cdot \lambda}{\beta \cdot \cos\theta}, \quad (1)$$

where λ is the X-ray radiation wavelength, β is the full width at the half maximum estimated after fitting of peaks with the Voigt function, and θ is the Bragg angle.

The experimental lattice constant (a) for the cubic structure was calculated by using the following formula:

$$a = d \cdot \sqrt{h^2 + k^2 + l^2}, \quad (2)$$

where d is the interplanar distance and h , k , and l are the Miller indices.

Raman measurements were conducted at room temperature in the air environment. A He-Ne laser with a 632.8 nm wavelength was used to excite Raman scattering. The laser power on the sample was 0.5 mW and the spot diameter was about 10 μm . Such conditions excluded any sample degradation or overheating. Spectra were collected in the range of 700–950 cm^{-1} , where characteristic Raman lines of different PVDF phases are located. The total acquisition time was 2 h for thicker samples (58 and 47 μm) and 5 h for thinner samples (20 and 15 μm).

For quantitative determination of α -, β -, and γ -phases, measurements were performed by Fourier-transform infrared spectroscopy using an FT-801 instrument (SIMEX, Novosibirsk, Russia) in absorption mode with a 4 cm^{-1} resolution.

The dielectric properties of the composite films were studied using an immittance meter (RLC) E7-30 (OJSC MNIPI, Minsk, Belarus). A 1 V electrical signal was applied to a 10 $\times$ 10 mm sample, covering frequencies from 100 Hz to 1 MHz. The composite film was sandwiched between two fiberglass plates coated with a 35-micron layer of sputtered copper. The real component of the permittivity, denoted as ϵ' , was determined using the specified following formula [26]:

$$\epsilon' = \frac{C \cdot t}{\epsilon_0 S}, \quad (3)$$

where C is capacity of thin film, t is the thickness of film, and S is the square of the contacts.

The magnetic measurements are presented in the Supplementary Materials.

3. Results and Discussion

According to the obtained electron microscopy data, the composite films have a thickness from 15 ± 0.7 to 58 ± 1.1 μm (Figure S1). Based on the obtained images of the films' surface, the diameters of spherulites and pores were estimated and are given in Table 1.

Table 1. Pore and spherulite diameters of PVDF-CFO composite films of different thicknesses.

Thickness (μm)	Average Spherulites Size (μm)	Average Pore Size (μm)
15	2.7 ± 0.3	1.2 ± 0.2
20	2.6 ± 0.3	1.3 ± 0.3
47	3.7 ± 0.5	2.5 ± 0.7
58	5.5 ± 1.2	2.6 ± 0.6

Figure 2 and Table 1 show that an increase in the size of spherulites and pores is observed in thick films. As the film thickness decreases, the growth and development of spherulites are constrained by the limited space, resulting in the formation of smaller and more widely distributed spherulitic structures. In contrast, thicker films allow polymer chains more space and time to form larger spherulites, while also exhibiting increased pore formation [27]. Additionally, the images presented show that MNPs tend to agglomerate in regions adjacent to the spherulites without penetrating into them.

The surface topology of the PVDF composites was studied using AFM. The surface roughness was quantified using the root mean square of the average flat surface (R_q), which is an average of the peaks reported in Table 2. AFM images of the surfaces of PVDF-CFO composite films of different thicknesses are shown in Figure S2. No dependence of roughness on film thickness was observed.

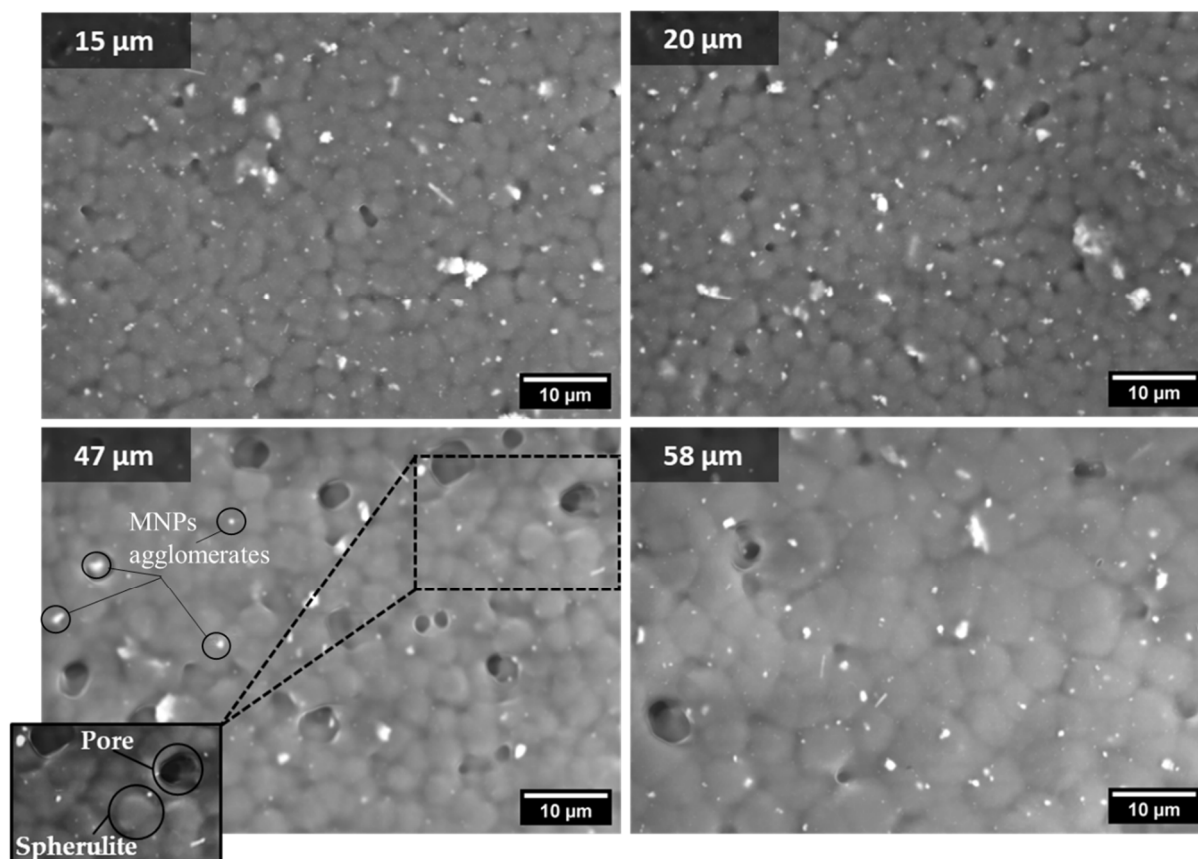


Figure 2. Surface structure of PVDF-CFO composite films with different thicknesses obtained by electron microscopy.

Table 2. Young's modulus, deformation, and root mean square roughness (R_q) of PVDF-CFO composite films of different thicknesses.

Thickness (μm)	Young's Modulus (MPa)	Deformation (nm)	R_q (nm)
15	29 ± 2	70 ± 3	132
20	33 ± 1	64 ± 1	125
47	30 ± 2	68 ± 3	162
58	45 ± 4	50 ± 1	127

The data obtained from SEM and AFM show that as the thickness of the composite films increases, the average size of spherulites and pores also increases. A sample with a thickness of 58 μm , in which the size of the spherulites is 5.5 μm , stands out. A significant increase in Young's modulus (45 MPa) is observed for this sample compared to other samples, where this indicator is in the range of 29–33 MPa. Apparently, there is a critical size of spherulite for this method, after which a rapid change in the mechanical properties of the surface occurs. XRD, Raman, and FTIR spectroscopy were performed to gain a more detailed understanding of how thickness affects the structural properties of the produced composites.

Based on the XRD results, the crystallographic structure of the MNPs was identified as cubic spinel with no detectable impurities [28]. The coherent scattering region associated with the average crystallite size is 15 ± 1 nm. Furthermore, the lattice parameter for the cobalt ferrite equal to $a = 8.37$ Å is close to the bulk value [29]. All the reflexes of the MNPs were indexed using Bragg's law (Figure 3a).

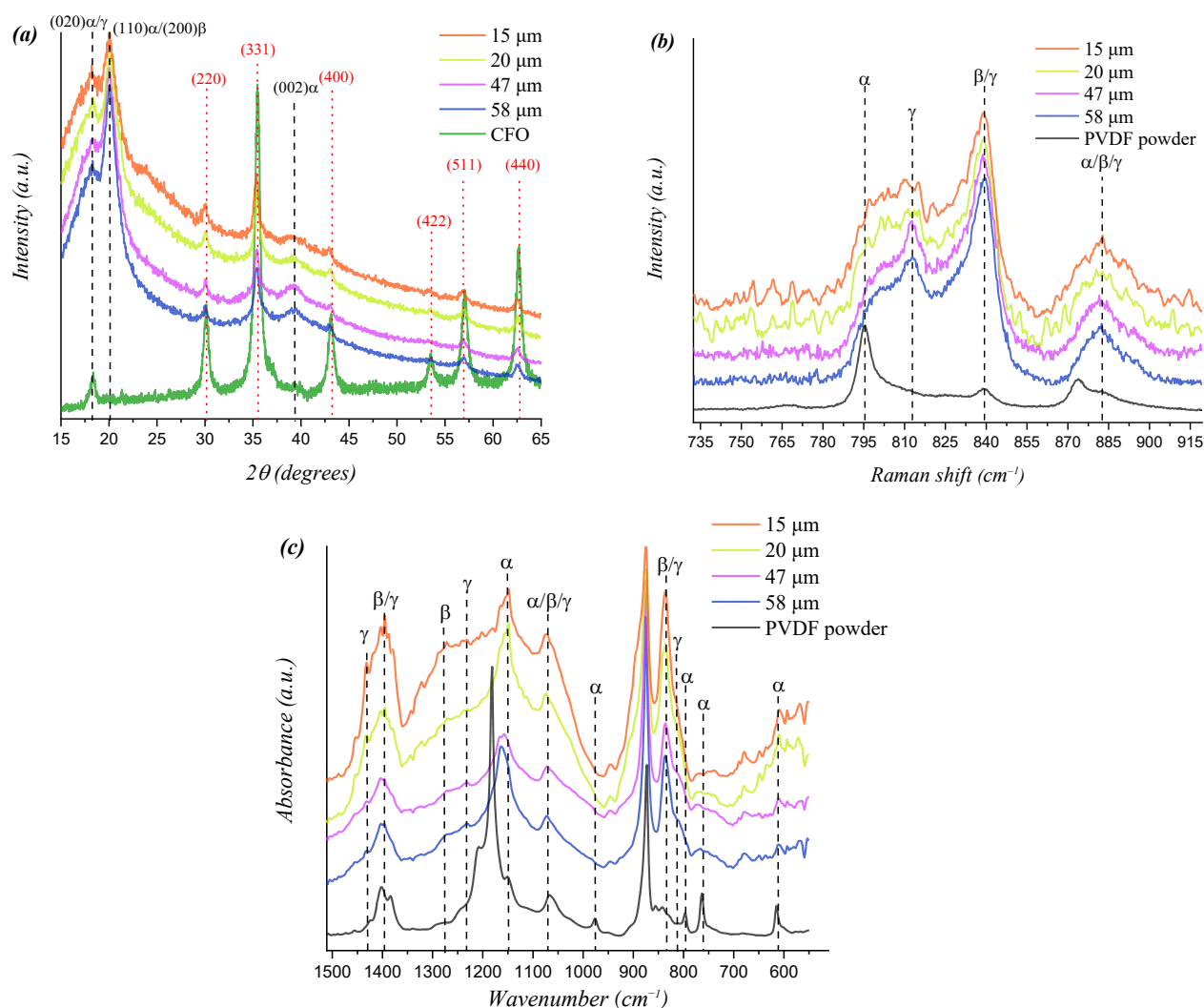


Figure 3. (a) X-ray diffraction pattern, (b) Raman spectra, and (c) FTIR spectra of composite PVDF-CFO films with different thicknesses.

For PVDF, we observed a reflex at $2\theta = 20.1^\circ$, corresponding to the superposition of diffraction in planes 110 and 200, which is characteristic of both the α - and β -phases of PVDF. In addition, the peak at $2\theta = 18.4^\circ$ corresponds to plane 020, which is indicative of the α - and γ -phases [30–32].

The Raman lines associated with the structural difference between the α -, β -, and γ -phases can be attributed to specific vibrational modes of the CH_2 group, such as rocking vibrations at 795 cm^{-1} for the α -phase and at 840 cm^{-1} for the β - and γ -phases and wagging vibrations at 812 cm^{-1} for the γ -phase, as shown in Figure 3b [33,34]. As depicted in the figure, the initial PVDF powder utilized in this study exhibited the α -phase. However, after the synthesis process, the γ - and β -phases formed in films, which is confirmed by the decrease in the intensity of the α -phase peaks and the increase in the β - and γ -phase peaks.

FTIR spectroscopy was used to quantify the content of the detected phases (Figure 3c). The quantification of the total electroactive phase ($F_{\text{EA}} = F_{\beta} + F_{\gamma}$) and individual β - and γ -phases was determined by the method proposed by Xiaomei Cai et al., which is based on the characteristic peaks for particular phases [35]. Thus, a clear absorption peak with a wave number close to 840 cm^{-1} manifests the presence of the electroactive β - and/or γ -phases, while the absorption peak at 763 cm^{-1} is associated with the non-electroactive α -phase. Then, the total electroactive phase was determined according to the following formula:

$$F_{EA} = \frac{I_{840}}{\left(\frac{K_{840}}{K_{763}}\right)I_{763} + I_{840}} \times 100\%, \quad (4)$$

where I_{840} and I_{763} are the experimentally obtained optical intensities at 840 cm^{-1} and 763 cm^{-1} , respectively, and K_{840} and K_{763} are the absorption coefficients at the corresponding wave numbers, whose values are 7.7×10^4 and $6.1 \times 10^4\text{ cm}^2\cdot\text{mol}^{-1}$, respectively.

The content of individual electroactive β - and γ -phases is determined according to

$$F(\beta) = F_{EA} \cdot \left(\frac{\Delta H_{\beta'}}{\Delta H_{\beta'} + \Delta H_{\gamma'}} \right) \times 100\%, \quad (5)$$

$$F(\gamma) = F_{EA} \cdot \left(\frac{\Delta H_{\gamma'}}{\Delta H_{\beta'} + \Delta H_{\gamma'}} \right) \times 100\%, \quad (6)$$

where $\Delta H_{\beta'}$ and $\Delta H_{\gamma'}$ are the differences in intensities between the peak at about 1275 cm^{-1} (specific for β -phase) and the nearest trough at about 1260 cm^{-1} and the peak at about 1234 cm^{-1} (specific for γ -phase) and the nearest trough at about 1225 cm^{-1} , respectively.

The calculated values of phase content in PVDF-CFO films of different thicknesses are presented in Table 3.

Table 3. Calculated values of phase content in PVDF-CFO films of different thicknesses.

Thickness (μm)	F_{EA} (%)	α -phase (%)	β -Phase (%)	γ -Phase (%)
15	87 ± 5	13 ± 5	42 ± 4	45 ± 4
20	80 ± 2	20 ± 2	29 ± 2	51 ± 2
47	69 ± 4	31 ± 4	4 ± 2	65 ± 4
58	75 ± 4	25 ± 4	5 ± 1	70 ± 4

The increase in peak intensity at 1275 cm^{-1} with decreasing thickness indicates an increase in the content of the electroactive β -phase (the change in the content of the total electroactive phase is presented in Figure 4). The decrease in thickness favors the formation of electroactive phase. The combined content of the β - and γ -phases—the electroactive phases—increases from 75% to 87%, while the α -phase content decreases from 25% to 13%. The β -phase content increases from 5% to 42% as the film thickness decreases from 58 to $15\text{ }\mu\text{m}$. Furthermore, this approach allows the value of the β -phase content to be slightly varied by controlling the thickness in the case of 15 and $20\text{ }\mu\text{m}$ composites. These results suggest that the electroactive phase is more prevalent in thinner composite films with smaller spherulites, which is likely to improve the alignment of dipoles in the polar phases, thus enhancing the electroactive properties of the material [36].

The phase composition, specifically the ratio of the α - and β -phases, is closely related to the dielectric properties of PVDF-CFO composites. The dielectric constant is a crucial factor for utilizing these fabricated films in sensors and energy devices. Thin films exhibit a higher content of the β -phase, which enhances their dielectric properties. An increased ϵ' can lead to improved energy storage capabilities, while a lower loss tangent (δ) means reduced energy dissipation during operation. By analyzing these properties at different thicknesses, the composites can be optimized for better performance in practical applications, such as magnetic field sensors and energy harvesters [37,38].

The dielectric parameters (permittivity and tangent loss) of the samples as a function of frequency at room temperature were measured (Figure 5). For all composite films, the dielectric constant decreases with increasing frequency. This trend is explained by the slow relaxation of electrical dipoles, which are unable to respond to fast changes in the

applied electric field at high frequencies [26,39]. Contrary to some works [17], the real part of the permittivity, ϵ' , decreases with increasing the film thickness. There are a number of factors that affect the dielectric properties, such as phase composition, filler shape and concentration, porosity, etc. [27,40]. Films with a higher β -phase content show increased ϵ' values in the frequency range up to 1 MHz. Conversely, an increase in the α phase content is associated with a decrease in ϵ' values [27]. In the present case, the increase in ϵ' is primarily explained by the increase in the ratio of the β - to α -phase and the reduced pore size of the polymer in thinner composite films.

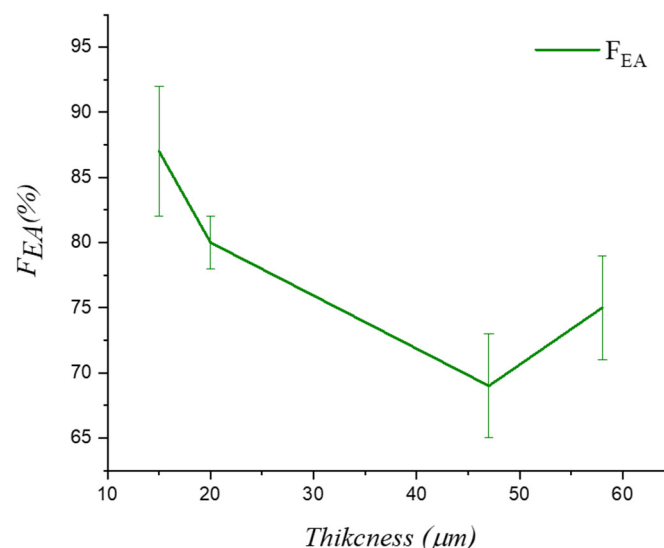


Figure 4. Variation of the content of total amount of electroactive phase ($F_{EA} = F_{\beta} + F_{\gamma}$) in PVDF-CFO composite films as a function of their thickness.

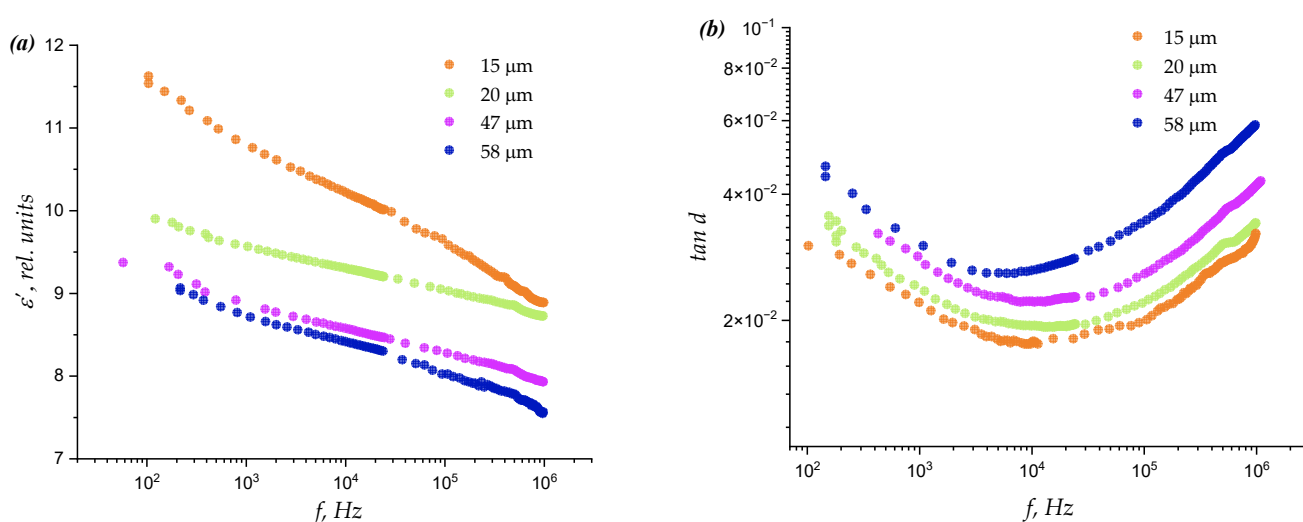


Figure 5. (a) Real part of the dielectric constant (ϵ') and (b) dielectric energy loss ($\tan(\delta)$) of PVDF-CFO composite films with different thicknesses.

4. Conclusions

In this study, the influence of the PVDF-CFO composite film thickness on the formation of the supramolecular structure (spherulites and pores), phase composition, surface topology, and mechanical and dielectric properties was investigated. The results indicated that as the thickness of the composite films decreased, the sizes of spherulites and pores also decreased. AFM analysis further revealed that the elasticity of the composite decreased

as the thickness dropped below 58 μm , with Young's modulus values of 45 ± 4 MPa for 58 μm and values of 29–33 MPa for films with thicknesses of 47, 20, and 15 μm .

X-ray diffraction and Raman spectroscopy confirmed the presence of both the electroactive β - and γ -phases, as well as the non-electroactive α -phase, across all samples. FTIR spectroscopy quantified the phase content, revealing that thinner films contained a higher β -phase and electroactive phases (42% and 87% vs. 5% and 75%). Additionally, it was found that the dielectric properties are improved in thinner films that contain more β -phases and fewer pores as opposed to thicker composite films. Our findings demonstrate a crucial role of thickness as key to the end route of PVDF-CFO composite films to high-level devices. The investigated effect of composite film thickness on material properties provides valuable insights that can be extrapolated to other analogous PVDF-based composite systems. The principles governing the relationship between the film thickness, phase composition, and dielectric properties are relevant to PVDF-based composites with similar structural and compositional characteristics.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst15010047/s1>, Figure S1: SEM images of cross-sectional of PVDF-CFO composite films with different thicknesses; Figure S2: Topography map of PVDF-CFO composite films of different thicknesses; Figure S3: The dependence of magnetization on the applied magnetic field for (a) CoFe_2O_4 MNPs; (b) nanocomposite PVDF-CFO films with thickness 15, 20, 47 and 58 μm . References [41–43] are cited in the Supplementary Materials.

Author Contributions: Conceptualization, P.A.V., V.D.S. and P.V.S.; methodology, P.A.V., V.D.S., V.V.S., S.A.V., P.V.S. and P.A.E.; formal analysis, S.A.V.; investigation, P.A.V., V.D.S., V.V.S., S.A.V., P.V.S. and P.A.E.; resources, V.V.R.; data curation, P.A.V., V.D.S., V.V.S. and P.A.E.; writing—original draft, P.A.V., V.D.S., A.S.O., P.V.S. and P.A.E.; writing—review and editing, A.S.O., L.V.P. and V.V.R.; visualization, P.A.V. and V.D.S.; supervision, V.V.R.; project administration, P.A.V.; funding acquisition, V.V.R. All authors have read and agreed to the published version of the manuscript.

Funding: The research was funded by the Russian Science Foundation under Project No. 21-72-30032.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding authors.

Acknowledgments: We thank the SHILI, a center for the identification, support, and development of abilities and talents of children and youth in the Kaliningrad region for the opportunity to carry out X-ray diffraction and SEM measurements.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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