

PVDF/PVDF-TRFE BLENDS LOADED WITH BATIO₃: FROM PROCESSING TO PERFORMANCE TESTING

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Abstract

Concerns surrounding the limited supply of fossil fuels have been the subject of much debate. As of promising solutions, polymers like poly(vinylidene fluoride) (PVDF) have gained attention due to their ability to generate electrical energy from the waste mechanical vibrations. The energy harvesting and vibration sensing potential of PVDF is however limited due to its low content of electroactive β -phase, which has to be increased by indirect post-processing. Recently, a synergistic effect was found in PVDF directly blended with its trifluoroethylene copolymer (PVDF-TrFE) due to strong interfacial polarization. In this study, we aim to further increment the piezoelectric performance of PVDF/PVDF-TrFE blends by incorporating a small amount of BaTiO₃ nanocrystals via a facile and scalable processing route. The β -phase content was monitored using FTIR and XRD. Melt rheology experiments showed that co-blending of PVDF-TrFE as well as the addition of BaTiO₃ slightly increased melt viscosity and complex modulus. Despite that, rheological data suggested that developed formulations can be processed by conventional techniques intended for a large-scale production. More importantly, PVDF/PVDF-TrFE binary blends supplemented with BaTiO₃ are expected to exhibit superior d33 compared to conventional neat blends, which could make them highly promising for modern energy harvesting and sensor-related applications.

Keywords: Nanohybrid, vibration sensing, PVDF, blending, d33, piezoelectricity

1. INTRODUCTION

The increasing demand for the electrical energy and depletion of fossil fuels are highly concerning facts of the present time [1]. The energy harvesting systems represent an alternative concept to address this challenge by converting the waste mechanical energy, such as vibrations, air/fluid movement, body motion etc., into the useful electrical form [2]. For this purpose, piezoelectric materials are well-suited since they spontaneously polarize when subjected to a mechanical stress [1,3]. Although the energy nanogenerators based on various inorganic materials (BaTiO₃, ZnO, InN, GaN, CdS) or ceramics (NaNbO₃, KNbO₃) have shown high piezoelectric coefficients, they are brittle, heavy and difficult to process [4]. These drawbacks can be eliminated/reduced by using ferroelectric polymers, mainly poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (PVDF-TrFE) [5] or hexafluoropropylene (PVDF-HFP) [6].

PVDF is a semi-crystalline polymer existing in five phases (α -, β -, γ -, δ - and ϵ -) depending on the processing routes and post-treatment. The α - and ϵ -phases are easily accessible directly from polymer melt [7], they are however non-polar due to *trans-gauche* conformation self-canceling the dipoles [5]. The γ - and δ -polymorphs are polar to some extent, and hence piezo- and ferroelectric [8]. While γ -phase PVDF is hardly accessible from α -phase using spatially confined systems; the α - to δ -phase changeover can be realized by so-called electroforming process under electric fields (~150 kV/mm) [5,8]. The most desirable phase for the construction

of energy harvesting and sensing devices, i.e. β -phase, can be obtained from α -phase by stretching (uniaxial or biaxial) at the elevated temperatures [9,10], and/or by polling of PVDF films under strong electric fields (above 500 kV/mm) [5, 11].

Contrary to PVDF, the copolymer PVDF-TrFE crystallizes directly into the electroactive β -phase regardless the processing conditions or post-treatment. Besides, PVDF-TrFE shows an increased chain mobility enabling to reach crystallinity of up to 90%, compared to PVDF that attains the maximal crystallinity of ~50% [5]. At present, the use of PVDF-TrFE is limited due to its complicated synthesis, which is reflected in high price, and relatively narrow working temperature range [12]. From these reasons, co-blending strategy was adopted to synergistically combine properties of the individual components. PVDF/PVDF-TrFE blends were found to be immiscible in the crystalline phase [13], however, their miscibility on the lamellar level was later confirmed due to co-existing mixed amorphous phase [14]. Meng et al. [5] found that minor amounts of PVDF-TrFE significantly increased β -phase content of PVDF, even beyond the rule-of-mixtures. This synergism with origins in the interfacial polarization resulted to a larger dielectric constant of PVDF/PVDF-TrFE when compared to pure components. Other strategy for enhancing the piezoelectric activity of PVDF is based on the incorporation of small amounts of various nanofillers [15,16] to maintain flexibility of the PVDF sensors, and even enhance their thermal stability [6].

Despite significant progress, a little attention has been paid to co-blended PVDF-based copolymers with inclusions of piezoelectric nanocrystals. Yang et al. [6] found that PVDF/PVDF-HFP blends loaded with dopamine-modified BaTiO₃ exhibited superior polarization level ($d_{33} = 40$ pc/N) compared to neat PVDF/PVDF-HFP blend ($d_{33} = 23$ pc/N), and obviously, neat PVDF ($d_{33} = 18$ pc/N). In this work, we aim to further increase the piezoelectric performance of PVDF/PVDF-TrFE blends by embedding the piezoelectric BaTiO₃ nanocrystals. The blending process was performed on a compounding device that allows the large-scale production. From the processing perspective, the rheological behavior of the binary blends as well as their BaTiO₃-loaded analogues was studied. Finally, the effects of PVDF-TrFE and BaTiO₃ on the formation of the electroactive β -phase content, and consequential d_{33} coefficient were investigated, implying a great potential of the developed nanocomposites.

2. EXPERIMENTAL PART

2.1. Materials

PVDF beads (CAS number: 24937-79-9, density of 1.78 g/cm³) having the average molecular weight (M_w) of 107 000 g/mol, PVDF-TrFE (Solvane®300/P300, CAS number: 28960-88-5, density of 1.90 g/cm³) with the composition of VDF and TrFE of 70 and 30 mol%, respectively, and BaTiO₃ nanopowder (CAS number: 12047-27-7, density of 6.08 g/cm³) were purchased from Sigma-Aldrich (USA).

2.2. Fabrication of nanocomposites

The desired amounts of PVDF and PVDF-TrFE were melt-blended using a micro-compounder DSM Xplore MC15 (Xplore Instruments, The Netherlands) at 240°C to produce binary blends with the weight ratios of 100/0 and 80/20. In parallel, analogous PVDF/PVDF-TrFE blends were fabricated containing 5 wt% of BaTiO₃ nanopowder. In a dosing sequence, the feedstock was gradually introduced into the compounder within 2 minutes at 25 rpm, followed by 10 minute blending at 40 rpm. A constant torque indicated homogeneity of the blends (and dispersion of the BaTiO₃). The product was collected in a form of filament.

Each filament was cut into pieces that were compression molded to produce films with a thickness of 0.5 mm. The calculated amounts of granules were placed into metallic molds, pre-heated for 5 minutes, and compressed with a pressure of 10 MPa for the additional 5 minutes, while temperature was set to 210 °C. Afterwards, the mold was cooled down in a controlled manner to ensure repeatability of the process.

2.3. General characterizations

The dimensions and morphology of BaTiO₃ was studied by transmission electron microscopy (TEM) on a JEM-2100Plus (JEOL, Japan) device equipped with a LaB6 cathode operating under the accelerating voltage of 200 kV. Prior to the analysis, the nanopowder was dispersed in acetone and dripped onto a carbon-coated TEM grid (300 mesh, Agar Scientific, UK). The TEM images were analyzed using ImageJ software (National Institutes of Health, USA).

The surface properties of BaTiO₃ were investigated through nitrogen adsorption/desorption isotherm collected on a volumetric gas adsorption analyzer (BELsorp Mini II, BEL, Japan) at 77K. The sample was degassed at 60 °C for 5 hours before starting the measurement. The specific surface area was determined by Brunauer-Emmett-Teller (BET) method using data points of relative pressure range from 0.05 to 0.30.

The Fourier transform infrared spectroscopy (FTIR) was performed on Nicolet 6700 (Thermo-Scientific, USA) spectrometer equipped with ATR accessory using a germanium crystal. The spectra were acquired in a wavenumber range of 4000-500 cm⁻¹ with a spectral increment of 2 cm⁻¹ at laboratory conditions.

The crystallographic structure of the samples was examined via X-Ray diffractions (XRD) using Miniflex 600 (Rigaku, Japan) diffractometer with a Co-K α radiation source ($\lambda = 1.789 \text{ \AA}$) operating within 2θ range of 10-95° with a scan speed of 3°/min.

Rheological behavior of the molten-state samples was studied on a Physica MCR502 (Anton Paar, Austria) rheometer equipped with the CTD600 heating chamber and TC30 temperature control unit. The complex viscosity was recorded during the frequency sweep from 0.1 to 100 Hz with a constant amplitude strain of 0.05 % at the temperature of 230 °C.

2.4. Vibration sensing assembly

Vibration sensing capability of the PVDF and PVDF-TrFE films and their BaTiO₃-loaded analogues was investigated on circular samples of 30 mm in a diameter and a thickness of 0.5 mm. Prior to the measurement, the poling of samples was performed at 100°C using a field of 20 kV/mm. The samples were pressed using a single-point bar; the applied mass equaled 400 grams and frequency of its oscillation was set to 1 Hz. The output signal was collected using NI-4331 resistance substitution box (National Instruments, USA) and the final d33 coefficients were calculated according to the equations described elsewhere [4,10].

3. RESULTS AND DISCUSSION

Although BaTiO₃ nanopowder is a commercial product, its relevant properties were studied to understand its implications on the structural and electromechanical characteristics of PVDF-based blends. **Figure 1a** shows its XRD pattern with a number of sharp peaks at 25.9° (001), 36.9° (101), 45.6° (111), 53.1° (002), 60.0° (102), 66.2° (112), 78.6° (202) and 84.3° (212) proving purity and crystalline character of the material (PDF Card No. 01-075-2121). The inset displays the size and morphology; the primary particles possessed rounded-shape with the average diameter of ~48±8 nm as determined by image analysis. The recorded physisorption isotherm curve was classified as reversible Type-II isotherm [17], and specific surface area calculated using BET method equaled 17 m²/g.

The FTIR spectra of the PVDF and PVDF/PVDF-TrFE films are displayed in **Figure 1b**. As seen, both spectra were almost identical and demonstrated the coexistence of β - and α -phase [18]. In more details, the data showed that the addition of the PVDF-TrFE incremented β -phase content, which was reflected in a higher intensity of β -peak around 841 cm⁻¹. At the same time, the intensity of α -peaks around 763 cm⁻¹ and 1210 cm⁻¹ diminished confirming the desirable phase transformation [5]. Therefore, binary PVDF/PVDF-TrFE blend was expected to achieve a superior piezoelectric performance. Such trend as not revealed in the FTIR spectra of BaTiO₃-loaded samples due to overlapping intensity coming from the filler.

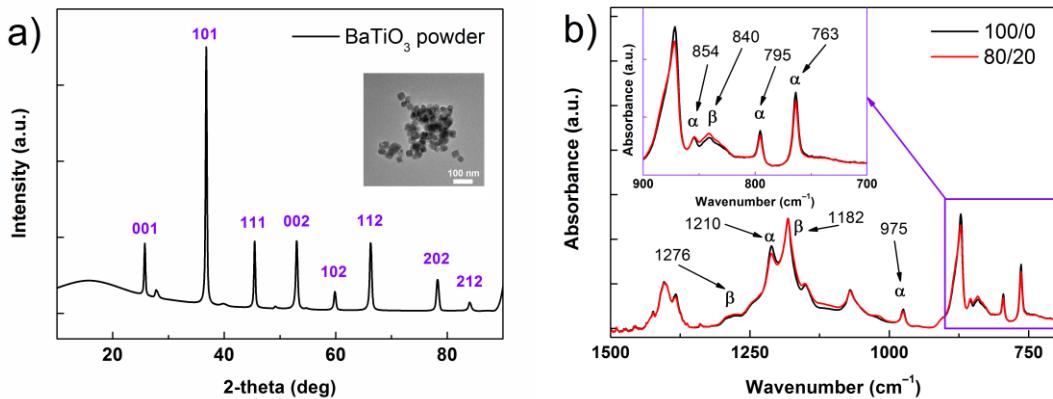


Figure 1 The XRD pattern (a) for BaTiO₃ nanopowder with inset TEM figure, and the FTIR spectra (b) for the neat PVDF and PVDF/PVDF-TrFE binary mixture.

The XRD analysis was used to determine the evolution of the crystalline phase in the samples. As seen in **Figure 2a**, the diffractogram ($K\alpha_1$, $\lambda = 1.790 \text{ \AA}$) of neat PVDF exhibited 2-theta peaks at 21.9° , 40.7° and 43.9° corresponding to β -phase, and a small peak around 42.1° related to α -phase. After the addition of PVDF-TrFE, the intensity of the β -peak signal at 21.9° dramatically increased, which demonstrated the ability of TrFE to spontaneously crystallize into this phase, regardless the post-treatment [5,10]. Moreover, the binary blend exhibited a significant development of α -phase corresponding to a double-peak at 19.4° and 20.1° ; the latter is sometimes associated also to γ -phase [18]. Introducing the BaTiO₃ nanopowder modified the XRD spectra (**Figure 2b**) and significantly affected the intensities of the PVDF-related peaks. By comparing the spectra, it appears that the crystalline phase was developed to a lower extent, when compared to the neat analogues. This phenomenon most likely occurred due to nano-confinement effects on polymer crystallization, since BaTiO₃ nanoparticles represent steric obstacles restricting the mobility of the PVDF chains [19]. Despite this effect, the PVDF/PVDF-TrFE blend loaded with BaTiO₃ exhibited remarkably higher β -peak intensity than its counterpart based on PVDF. The rest of the XRD spectra (2-theta above 28°) resembled the pattern for BaTiO₃ nanopowder.

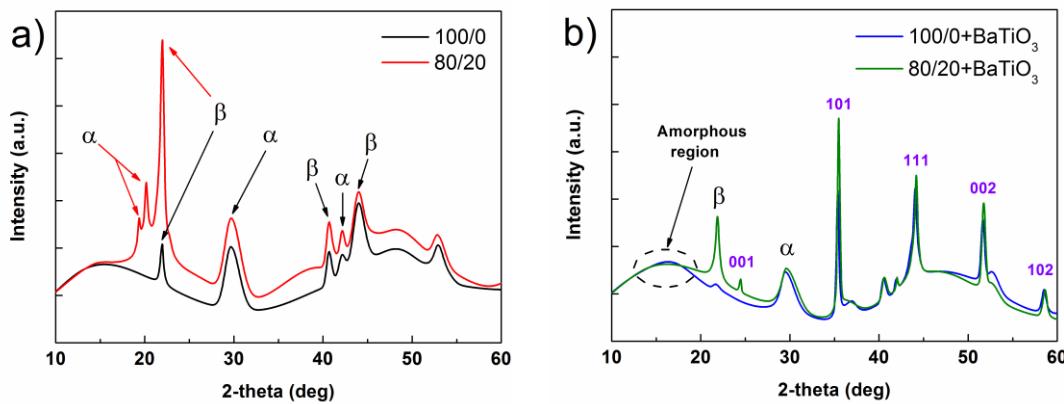


Figure 2 XRD patterns for PVDF and PVDF/PVDF-TrFE blends (a) and their BaTiO₃-loaded analogues (b).

Rheological study was employed to gain a useful insight to the processing ability of the PVDF-based systems and the results are shown in **Figure 3**. It was found that storage modulus, G' , and complex viscosity, η^* , values of PVDF/PVDF-TrFE blend were higher than those of neat PVDF, which was attributed to a higher polarity of the former providing stronger interactions, and thus more resistance to flow [20]. The addition of BaTiO₃ nanocrystals further increased the G' and η^* values due to well-known stiffening effects of rigid inorganic particles when dispersed in polymer matrix.

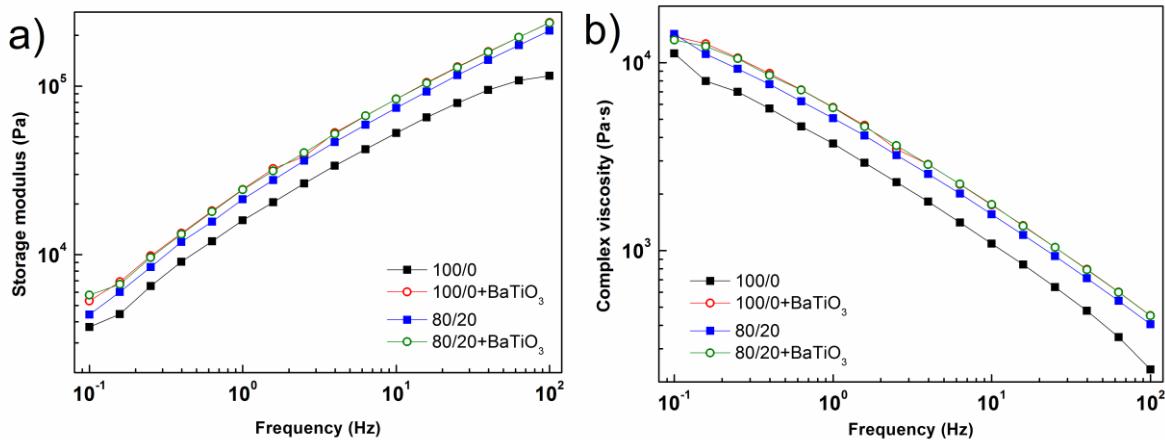


Figure 3 The melt rheology data for the PVDF and PVDF/PVDF-TrFE blends (solid symbols) and their BaTiO₃-loaded analogues (open symbols) represented as storage modulus (a) and complex viscosity (b).

The electromechanical capability of the PVDF-based elements can be predetermined by the β -phase content [11] and the presence of nanofillers [6], besides the other relevant factors [10]. **Table 1** displays the recorded d33 values for the investigated samples. As seen, the PVDF/PVDF-TrFE blend exhibited a superior d33 coefficient when compared to the neat PVDF due to the ability of PVDF-TrFE to crystallize directly into the β -phase [5], which correlates well with the XRD pattern (**Figure 2a**). The addition of BaTiO₃ nanopowder further enhanced d33 values (by 23.6 % and 41.7 %, respectively, compared to neat analogues), which stems from its inherent piezoelectric character. From these reasons, the PVDF/PVDF-TrFE with BaTiO₃ inclusions exhibited the highest d33, and thus, the best vibration sensing and energy harvesting capability among the samples. It is presumed that further improvements could be achieved by increasing the concentration of BaTiO₃ nanocrystals.

Table 1 The d33 values for the PVDF and PVDF/PVDF-TrFE films and their BaTiO₃-loaded analogues

Sample ID	100/0	80/20	100/0 + BaTiO ₃	80/20 + BaTiO ₃
d33 (pC/N)	14.8±1.7	15.1±1.4	18.3±1.1	21.4±0.7

4. CONCLUSION

In this work, the processing and energy harvesting capabilities of the neat PVDF, PVDF/PVDF-TrFE blend, and their BaTiO₃-loaded analogues were investigated. The materials were fabricated using industrially scalable techniques, such as compounding and compression molding. The FTIR showed that binary blend exhibited a higher content of the electroactive β -phase, without any additional interventions or post-processing. The XRD analysis confirmed the presence of β -phase via characteristic signal at 21.9°, and also, a minor content of α -phase at 19.4° and 20.1°. The intensity of these peaks was attenuated in BaTiO₃-loaded analogues, most probably, due to nano-confinement effects on polymer crystallization. The co-blending of PVDF-TrFE and the presence of BaTiO₃ nanocrystals resulted to increased G' and η^* values, but these factors synergistically enhanced d33 coefficient up to 21.4±0.7 pC/N, which is highly relevant for intended applications.

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