

## THE EFFECTS OF MOLECULAR AND PROCESSING PARAMETERS ON ENERGY HARVESTING CAPABILITY OF PVDF-BASED NANOGENERATORS

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### Abstract

In the research of the alternative vibration sensing systems, the major potential is attributed to piezoelectric materials that can generate the electrical output from the waste vibration sources of the industrial machines. Poly(vinylidene fluoride) (PVDF), mostly in the electroactive  $\beta$ -phase, is a great option due to its excellent piezoelectric properties and good flexibility. The  $\beta$ -phase PVDF can be obtained by simple stretching of the  $\alpha$ -phase PVDF films, and the conditions of this process are well documented. Surprisingly, the implications of molecular parameters of the PVDF have not been addressed yet. This study investigates the effect of the molecular weight (Mw) of the PVDF on the  $\beta$ -phase development and consequential vibration sensing capabilities after uniaxial stretching. The successful phase transformation was confirmed using FTIR and XRD. In the FTIR spectra, a typical  $\alpha$ -phase peak at  $762\text{ cm}^{-1}$  diminished giving rise to the  $\beta$ -phase peak at  $840\text{ cm}^{-1}$  after the stretching. The results also showed a remarkable impact of the Mw on d33 coefficient making Mw an important parameter that should not be overlooked in designing the PVDF-based sensing elements. The obtained data are highly important for the optimization of the PVDF-based vibration sensors applicable in the efficient structural and health monitoring nanosystems.

**Keywords:** Nanosystem, vibration sensing, poly(vinylidene fluoride), crystallites, d33, electromechanical coupling

### 1. INTRODUCTION

At the present time, the increasing demand for the electrical energy is one of the most serious challenges that world faces. To cover this demand, fossil fuels, such as petroleum, coal and natural gas, are used as the main primary-energy source. The use of these traditional fuels is however connected to many environmental problems including air pollution, water pollution, or accidental oil spills [1,2]. From these reasons, there is an urgent need for the alternative energy sources. Probably, the most fascinating alternative concept to obtain energy is represented by the energy harvesting systems. Such devices utilize waste mechanical energy, such as vibrations, air/fluid movement, body motion etc., and converts it into the electrical form [3]. To construct the energy harvesting nanogenerator, various inorganic semi-conducting materials (ZnO, InN, GaN, CdS) or free ceramics (NaNbO<sub>3</sub>, KNbO<sub>3</sub>) have been studied [4]. Although these materials demonstrated high efficiency, they are brittle, heavy and difficult to process, which limits the breadth of applications [3,5]. To eliminate these drawbacks, the materials of choice can be found in ferroelectric types of polymers, mainly poly(vinylidene fluoride) (PVDF) and its copolymers [6]. PVDF is a polymorphic material existing in five phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ ) depending on the processing methods. The  $\alpha$  and  $\epsilon$ -phases are non-polar due to the antiparallel packing of dipoles. On the other hand, the  $\beta$ ,  $\gamma$  and  $\delta$ -phase are polar, and hence electroactive [7]. The  $\gamma$ -phase of PVDF is referred to as the mixture of the  $\alpha$  and  $\beta$ -phases, while  $\delta$ -phase is regarded as polar version of  $\alpha$ -phase. Amongst all conformations, the  $\beta$ -phase PVDF is the most desirable one for the construction of the

energy harvesting and vibration sensing devices, since it exhibits the best piezoelectric properties [8,9]. The significant research efforts have been therefore targeted to facilitate formation of the  $\beta$ -phase content in PVDF. The  $\beta$ -phase can be obtained directly from the polymer melt, however, the process requires high temperature, high pressure and other specific conditions [9]. Conversely, the  $\alpha$ -phase can be obtained very easily, because it is the most stable primary phase of PVDF [10]. And subsequently, it can be transferred into the  $\beta$ -analogue by simple stretching (uniaxial or biaxial) at the elevated temperatures [11]. Other method to increment the  $\beta$ -phase content is through poling of the PVDF films in high external electric fields [12]. Also, the fabrication of films through electrospinning, which is also a form of mechanical elongation, was successfully applied [13]. Certain improvements in the  $\alpha$ - $\beta$ -phase transformation were observed after the addition of graphene oxide or cellulose particles [14,15]. The  $\beta$ -phase is also achievable from the  $\gamma$  and  $\delta$ -phase using a plethora of other processing techniques [9,16]. However, from the technological point of view, the uniaxial stretching is the most convenient method to convert the  $\alpha$ -phase into its electroactive  $\beta$ -counterpart. The stretching process of the PVDF was performed within wide temperature range (50–150 °C), with different stretching speeds (1–1000  $\mu\text{m/s}$ ) and various (1–5) stretching ratios [10]. Although the effects of these parameters on the formation of  $\beta$ -phase PVDF have been described, the implications of its molecular weight ( $M_w$ ) on the  $\beta$ -phase development, energy harvesting and vibration sensing capabilities have not been, surprisingly, addressed yet. Moreover, the  $M_w$  of the applied PVDF is hardly ever mentioned in the literature. This paper therefore aims to clarify the correlations between the  $M_w$  of the PVDF and the formation of the electroactive  $\beta$ -phase and consequential  $d_{33}$  coefficient after stretching at various uniaxial ratios.

## 2. EXPERIMENTAL PART

### 2.1. Materials

The PVDF beads (CAS number: 24937-79-9) of different average molecular weights ( $M_w$ ); 71 000, 107 000 and 530 000 g/mol (sample ID: M71, M107 and M530) were purchased from Sigma-Aldrich (USA). The density of beads was 1.78 g/cm<sup>3</sup> and they were used as received.

### 2.2. Fabrication and stretching process

The PVDF films with thickness of 0.8 mm were prepared using compression molding. In a typical procedure, the calculated mount of PVDF beads was placed into a mold, pre-heated (5 minutes) and compressed with a pressure of 10 MPa (for additional 5 minutes), while the temperature was set to 210 °C. Afterwards, the mold was cooled down in a controlled manner to ensure repeatability of the process. The characterization/testing of the samples was performed at least 24 h after their successful fabrication.

The rectangular strips (dimensions of 10 mm × 100 mm) were cut out from PVDF films. Stretching of as-prepared PVDF elements was performed using a tensile device M350-5 CT (Testometric, Lancashire, UK) coupled with a heat chamber (Omron) operating at a temperature of 65 °C. The cross-head speed of the clamps was set to 10 mm/min, with the relative elongations of 50, 100, 200, 300 and 500 %. In the case of M71, the elongation of 500 % could not be achieved, since it was above its breaking point. Therefore, for this sample, we have selected the maximum elongation at 400 %.

### 2.3. General characterization

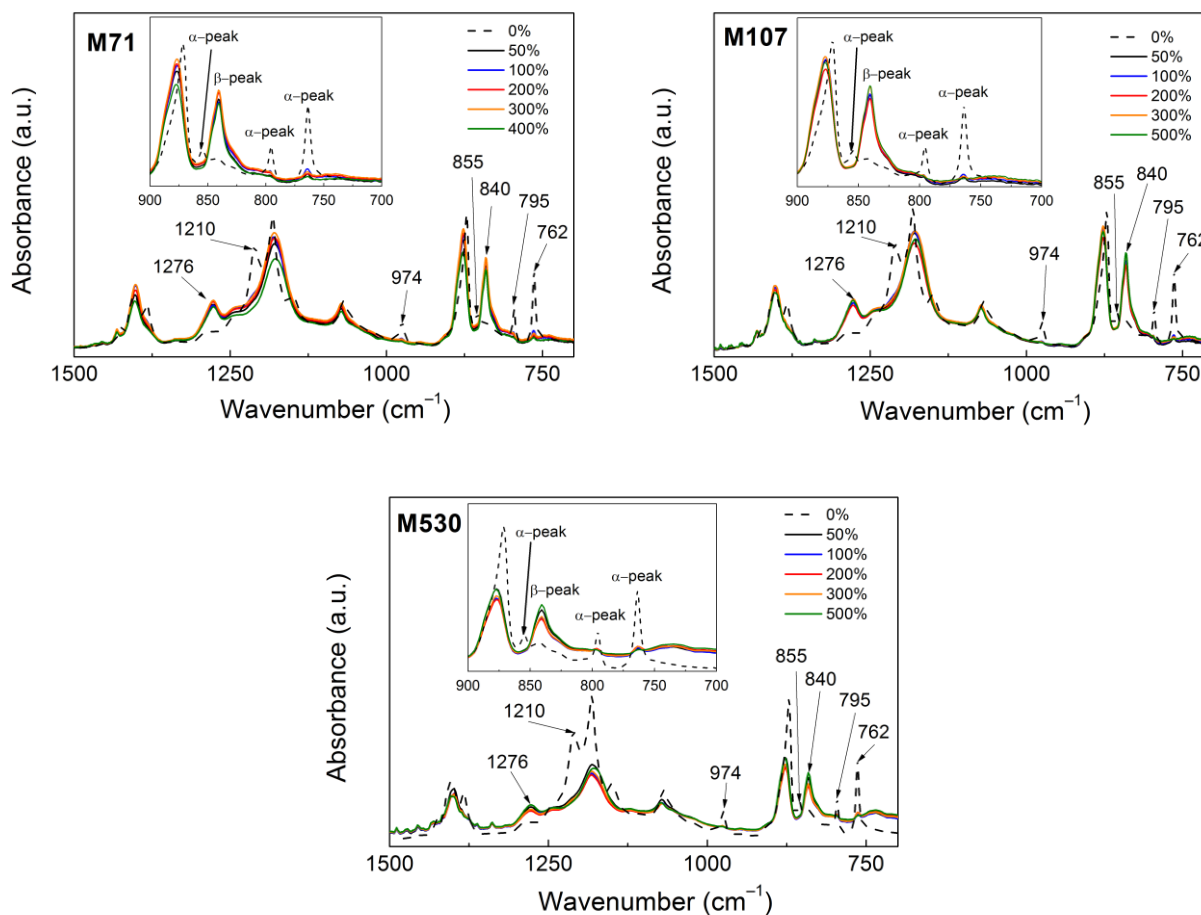
The crystalline phase development of PVDF films was studied via X-Ray diffractions (XRD) using Miniflex 600 (Rigaku, Japan) diffractometer with a Co-K $\alpha$  radiation source ( $\lambda = 1.789 \text{ \AA}$ ) operating within  $2\theta$  range of 10–95° with a scan speed of 3°/min. The Fourier transform infrared spectroscopy (FTIR) was performed on Nicolet 6700 (Thermo-Scientific, USA) spectrometer equipped with ATR accessory and a germanium crystal. The spectra were recorded in a wavenumber range of 4000–500 cm<sup>-1</sup> with a spectral increment of 2 cm<sup>-1</sup>. Both analyzes were performed at laboratory conditions.

## 2.4. Energy harvesting setup

Firstly, the poling of the stretched PVDF strips was performed using a custom-build apparatus at the electric field strength of 7 kV/mm, and the temperature of 110 °C. Secondly, a thin conductive (silver) layer was deposited on the samples and their piezoelectric charge coefficient,  $d_{33}$ , was measured within one hour after the poling process. The  $d_{33}$  was analyzed in the transversal mode using the electrometer 6517b (Keithley, USA). Each sample was placed between two copper electrodes; the lower electrode had a diameter of 20 mm, while the upper one had a diameter of 10 mm. A mechanical force of 0.49 N was applied onto the upper electrode and the electric charge generated by the sample was recorded. Each sample was analyzed at ten positions, the presented  $d_{33}$  values represent the average values from the obtained data.

## 3. RESULTS AND DISCUSSION

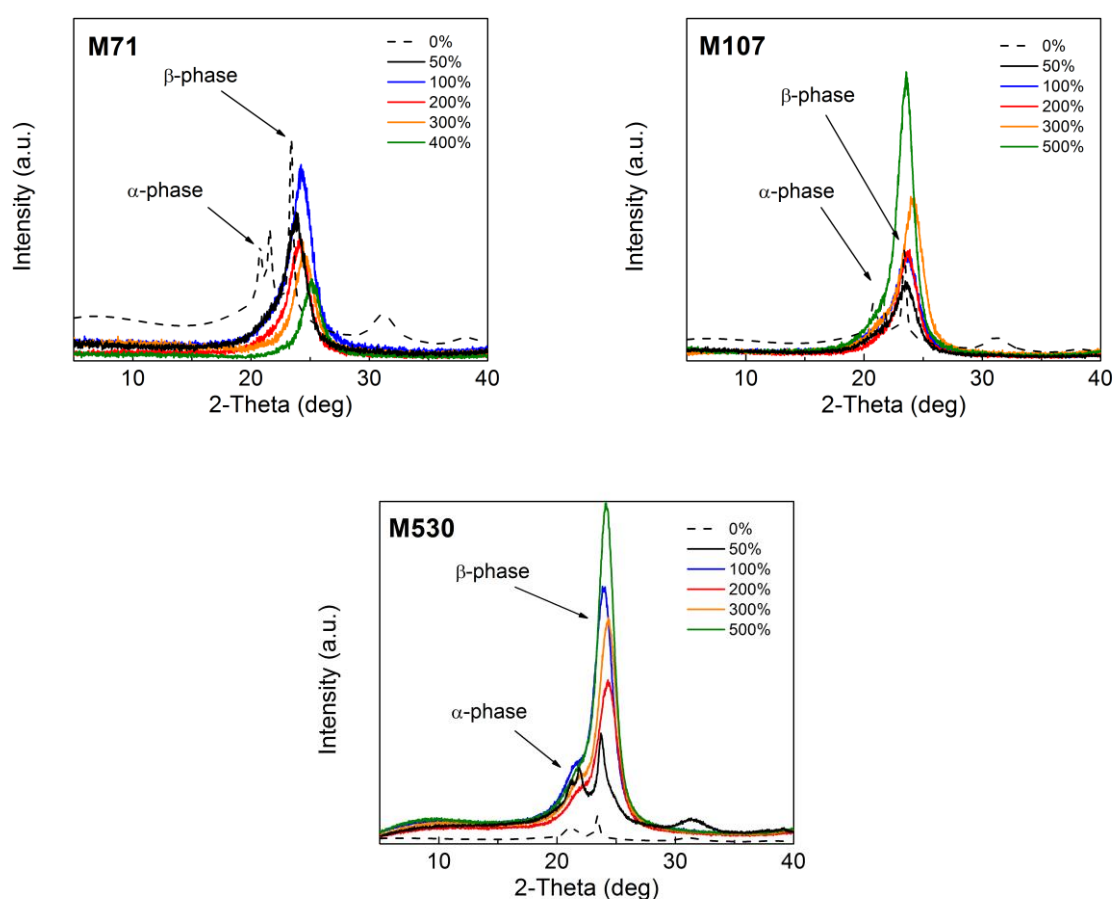
The PVDF strips of different  $M_w$  were stretched at the temperature of 65 °C to generate the piezoelectric  $\beta$ -phase with subsequent poling process performed at 110 °C. The efficiency of phase transformation was determined by means of the FTIR spectroscopy. **Figure 1** compares the FTIR spectra recorded for the M71, M107 and M530 samples. As clearly seen, the mechanical stretching significantly altered the FTIR profile indicating changes in the polymer chain conformations. In detail, the  $\alpha$ -phase PVDF can be identified through a large number of characteristic peaks. In the studied wavenumber region, the relevant peaks of the  $\alpha$ -phase were centered at 762, 795, 855, 974 and 1210  $\text{cm}^{-1}$  [2,17]. After stretching, these peaks diminished giving rise to their electroactive  $\beta$ -phase counterparts centered at 840 and 1276  $\text{cm}^{-1}$  [11].



**Figure 1** Comparison of the FTIR spectra for the PVDFs of different  $M_w$

The interpretation of peak at  $840\text{ cm}^{-1}$  is not always straightforward; in some papers this peak is classified as pure  $\beta$ -phase [17], while in others it is considered as the  $\beta$ - $\gamma$ -phase mixture [18]. However, the signature of the  $\gamma$ -phase in terms of peaks at  $776$ ,  $812$ ,  $833$  and  $1233\text{ cm}^{-1}$  was not identified. Also, the peak at  $840\text{ cm}^{-1}$  was sharp without any distinct shoulder that would be coming from the  $\gamma$ -phase. Based on these findings, we tend to believe that the content of the  $\gamma$ -phase in the PVDF was rather minimal.

The XRD is usually used as a complementary technique to determine the crystal phase of the PVDF. As shown in **Figure 2**, all samples exhibited typical XRD diffractograms ( $K\alpha_1$ ,  $\lambda = 1.790\text{ \AA}$ ). Prior to stretching, the  $\alpha$ -phase was the most prevailing and exhibited typical double-peak corresponding to diffractions in planes (100) and (020), respectively. After the stretching, the  $\beta$ -phase was successfully developed, which was reflected in the single sharp peak that is assigned to the total diffraction in (110) and (200) planes [13]. The phase transformation was remarkably affected by the  $M_w$  of the samples. For M71, the manifestation of the  $\beta$ -peak changed without any trend in peak intensity. In the samples M107 and M530, the intensity of the  $\beta$ -peak generally increased with the relative elongation, which implies a greater efficiency of the  $\alpha$ - $\beta$ -phase transformation. These results indicate that the  $M_w$  of the PVDF has a significant influence on the structural changes during the stretching process.



**Figure 2** Comparison of the XRD patterns for the PVDFs of different  $M_w$

The electromechanical performance of the PVDF mainly depends on the  $\beta$ -phase content [12]. In our case, the formation of the  $\beta$ -phase was facilitated by stretching in a combination with poling process. **Table 1** summarizes the  $d_{33}$  data for the investigated samples. It can be claimed that the applied stretching positively affected the  $d_{33}$  values, since they increased by a factor of 4–5 for the M71 and M530, when stretched from 50 to 500 % relative elongation. The highest  $d_{33}$  value was however detected for the M107, which exhibited

the  $d_{33}$  of 9.10 pC/N at maximal relative elongation. This value is below the theoretical  $d_{33}$  maximum that is over 25 pC/N for pure  $\beta$ -phase PVDF. Such difference indicates the persistent co-existence of the  $\alpha$ -phase, and the presence of trapped charges induced during the processing [19]. It should be mentioned that samples M107 and M530 have potential for further improvements since they have capability to achieve even higher relative elongations, and thus better conditions for the  $\beta$ -phase development. To conclude, we have shown that the  $M_w$  of the PVDF is highly important parameter affecting the  $d_{33}$  performance, and thus, it is of high relevancy for the fabrication of vibration sensing and energy harvesting elements.

**Table 1** Summarized  $d_{33}$  values for the investigated PVDF samples

Sample ID	50 %	100 %	200 %	300 %	500 %
M71	1.20 pC/N	5.10 pC/N	5.62 pC/N	6.20 pC/N	*6.50 pC/N
M107	7.00 pC/N	7.80 pC/N	7.60 pC/N	8.50 pC/N	9.10 pC/N
M530	2.00 pC/N	4.18 pC/N	3.20 pC/N	3.60 pC/N	8.20 pC/N

\*the value taken for sample with the relative elongation of 400 %

#### 4. CONCLUSION

In this study, the PVDF strips of different  $M_w$  were stretched and subjected to poling in order to facilitate formation of the piezoelectric  $\beta$ -phase. The phase transformation was monitored using FTIR spectroscopy demonstrating the changeover between the dominating peaks of the  $\alpha$  and  $\beta$ -phase at 762  $\text{cm}^{-1}$  and 840  $\text{cm}^{-1}$ , respectively. Also, the XRD data showed the successful  $\beta$ -phase development. In particular, samples M107 and M530 exhibited increasing peak-signal intensity with the relative elongation. The implications of different  $M_w$  of the samples were reflected in the  $d_{33}$  values that exhibited significant variations. Samples M71 and M530 experienced several-fold increase in the electromechanical performance, however, the highest value of the  $d_{33}$  was 9.10 pC/N generated by the M107. Based on these preliminary findings, further research is clearly required to better understand the interrelations among the  $M_w$ , relative elongation, crystallinity, poling conditions and  $d_{33}$  value of the PVDF-based nanosystems.

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