Abstract

In this contribution, the effect of the extrusion process of the poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) with the subsequent elongation/poling on its structural and dielectric properties is presented. The extrusion can be understood as continuous processing of polymer melts in the large scale (in comparison to solvent casting), when the thickness of the final product can be varied depending on the final operation conditions. Herein, the PVDF-co-HFP sheets of 5 cm in width were extruded using a single screw extruder. The fabricated sheets were cooled down and then, they were cut to the stripes and subsequently stretched to various elongations (100, 200 and 500 %) using a universal tensile testing machine. Such samples were investigated using FTIR in order to determine the effect of the elongation process on the transformation of the α-phase to the β-crystalline phase. The extend of the electro-active β-phase was quantified and its impact on the dielectric properties was investigated. The results clearly demonstrated that the elongation has a crucial effect on the final dielectric properties of the PVDF-co-HFP.

Keywords: Poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropylene), extrusion, dielectric properties, electromechanical coupling

1. INTRODUCTION

Smart systems can be classified as materials that can actively respond to the external stimuli, such as the electric [1] or magnetic field [2], temperature [3], pH change [4], light stimulation [5] or mechanical vibration [6]. In the last years, the majority of the electrical machines undergo the damaging due to the vibrations from the bearings causing the mechanical perturbances [7]. Therefore, the detection of the unwanted vibrations seems to be a crucial point to extend the operating lifetime of the machines. From this point of view, the vibration sensors based on the piezoelectric ceramics are typical materials of choice [8]. The ceramic-based sensors however have some drawbacks such as high cost and brittleness [9]. Especially, the brittleness is a very negative property, which can significantly decrease the efficiency of this type of sensor [10].

Therefore, certain polymeric materials such as poly(vinylidene fluoride) (PVDF) started to be very attractive, since they can be easily processed, they are flexible and provide suitable piezoelectric capability required for the vibration sensing [11]. The main issue of the PVDF is its inherent property; the materials requires the additional treatment, otherwise the PVDF consist mainly the non-piezoelectric α-phase [12]. By utilizing the elongation [13], polling in electric fields [14], particle addition [15] etc., the piezoelectric β-phase can be developed, and relatively good electromechanical coupling coefficients ($d_{33} \sim 25 \text{ pC/N}$) can be achieved [16].
There are also other techniques of the PVDF post-processing that were successfully applied to increment the $d_{33}$ coefficients including the electrospinning [17], melt-electrowriting [18] or the extrusion [19].

Besides the PVDF, also its copolymers are very promising for this purpose. The poly(vinylidene-co-hexafluoropropylene) (PVDF-co-HFP) is frequently used due to its good piezoelectric capability [20]. Its processing via the extrusion is however very limited, and just few research articles have addressed this topic [21], while only one paper was dealing with stretching during poling called SSP [22]. In the vast majority, this material is processed by solvent casting [23] or electrospinning [24]. From these reasons, this study is focused on the processing of the PVDF-co-HFP using industrially-viable extrusion process, and the impact of various relative elongations on the structural changes and dielectric properties.

2. EXPERIMENTAL

2.1. Materials

Poly(vinylidene-co-hexafluoropropylene) (PVDF-co-HFP) in the form of pellets (CAS number: 9011-17-0) with the molecular weight (Mw) of ~ 400 000 g/mol (Sigma Aldrich, USA) was used to construct the tested elements.

2.2. Characterization methods

The extrusion process was performed at 190°C using twin-screw extruder (Scientific, China) and using flat die having 5 cm in width and 0.5 mm in thickness. The continuous sheet was collected and cooled down without any interventions at laboratory conditions.

Then, the sheets were cut using the steel templates to the form of stripes with 15 mm in width, 100 mm in length. Such stripes were elongated using the universal testing machine 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 and 300 %.

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$^{-1}$ with a spectral increment of 2 cm$^{-1}$.

Dielectric properties were measured on the neat as well as on the stretched samples using Broadband Dielectric Impedance Analyzer (Novocontrol, Montabaur, Germany), in the frequency range of 0.01 Hz to 10 MHz, using a standard sample cell BDCS 140.

The neat PVDF-co-HFP as well as the stretched analogues were poled using a custom-build apparatus at the electric field strength of 7 kV/mm, and the temperature of 110 °C. Then, a thin conductive (silver) layer was deposited on the samples and their piezoelectric charge coefficient, $d_{33}$, was measured within 24 hour after the poling process. The $d_{33}$ was measured 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-co-HFP has similar crystalline structure as the neat PVDF. For this material, the transformation of α-phase to β-phase also plays a crucial role [25-27]. The typical main peaks of the α-phase corresponding to 762 cm$^{-1}$ and for the β-phase at 840 cm$^{-1}$ as displayed in Figure 1. A magnified visualization (inset figure) provides definite information of the successful α-β-phase transformation. As clearly seen, neat PVDF-co-HFP shows a negligible peak at 840 cm$^{-1}$ and with further elongation this peak clearly increases exhibiting the
highest intensity for the sample with 300 % deformation. On the other hand, the suppression of the $\alpha$-phase is similarly important. In this case, the visible decrease of the peak intensity and thus confirmation, that $\alpha$-$\beta$-phase transition was successful, was easily distinguishable only for the sample with the elongation of 300 %. The other samples did not exhibit almost any changes in the $\alpha$-peak intensity, while slight decrease was observed for the sample that underwent the elongation of 100 %. This clearly indicates that extrusion process with consequent elongation has crucial impact on the distribution of the micro and nano-sized crystallites those presence is very important for development electro-active $\beta$-phase. Similar observation was also published on PVDF samples [28].

Dielectric properties are assumed to be a crucial parameter affecting the electro-activity of the PVDF-co-HFP-based elements. Therefore, the relative permittivity was plotted against frequency; as obvious, the higher relative permittivity is achieved, therefore the better electrical output efficiency upon mechanical stimulation can be generated [29,30]. As can be seen in Figure 2, the relative permittivity measured on the prepared samples was increasing with the increasing deformation. This behavior demonstrates that the transformation of the $\beta$-phase was successful which is presented as a substantial increase of relative permittivity with higher strain deformation, and in fact, it confirms the trends obtained from the FTIR analysis.

**Figure 1** FTIR spectra of the PVDF-co-HFP samples before and after stretching process

**Figure 2** Dielectric spectra of relative permittivity against frequency of the PVDF-co-HFP samples before and after stretching/poling process
Finally, the electromechanical activity of the investigated samples is presented in Table 1. The dataset confirms that the industrially extruded PVDF-co-HFP samples can be effectively treated to increment their piezo-activity via elongation and subsequent polling process at 7 kV/mm. The maximal $d_{33}$ values obtained for these materials upon the presented conditions are sufficient to show a comparable efficiency with the other commercial PVDF systems [31].

Table 1 Results of the piezo-activity for PVDF-co-HFP-based samples

| Sample ID          | Capacitance (pF) at 100 kHz | $d_{33}$ coefficient (pC/N) | $d_{33}^2/e_{33}$ |
|--------------------|------------------------------|-----------------------------|-------------------|
| neat PVDF-co-HFP   | 6.19                         | 1.1                         | 3.47              |
| PVDF-co-HFP 50 %   | 11.6                         | 1.8                         | 7.22              |
| PVDF-co-HFP 100 %  | 11.8                         | 1.9                         | 8.11              |
| PVDF-co-HFP 300 %  | 12.6                         | 4.6                         | 37.1              |

$^a$ permittivity $e_{33} = C \times h/A$, where $C$ is the capacitance, $h$ is the sample thickness, and $A$ is the surface area.

4. CONCLUSION

In this paper, the PVDF-co-HFP was extruded and further elongated using various deformations (50, 100, and 300 %). Then, the materials were poled and investigated from their electro-activity point of view. It was confirmed that the elongation positively influenced the transformation of the non-piezoelectric $\alpha$-phase to its piezoelectric $\beta$-phase analogue, which was accompanied by increasing FTIR peak centered at 840 cm$^{-1}$. Analogously, the dielectric properties, specifically, the relative permittivity also increased with the elongation factor. Finally, the electromechanical investigation proved that $d_{33}$ coefficient, and thus the effectivity of the systems was incremented, which was attributed to successfully developed $\beta$-phase. The most significant enhancement (4-fold) of $d_{33}$ was recorded for the PVDF-co-HFP elongated by 300 %. Finally have to be concluded, that extrusion process and consequent elongation positively influencing the distribution of the micro and nano-sized crystallites to form proper $\beta$-phase enhancing the vibration sensing effectivity for sample elongated by 300%.

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