Metal-organic structures as additives in polyvinylidene fluoride

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Abstract—This paper describes the synthesis and characterization of the first-ever combination of polyvinylidene fluoride (PVDF) semi-crystalline polymer and iron-based metallic-organic structures (MOF). The resulting specimens were made in the form of thin fibers. It is assumed that thanks to these additives in the form of nanoparticles, the performance of PVDF nanofibers can be enhanced in the future. Both components can currently be considered as emerging materials. This is the initial successful production and presentation of results obtained by electron microscopy (SEM), Raman spectroscopy, and Fourier transform infrared spectroscopy (FTIR). These methods provided a basic overview and compared the differences in sample morphology and different phase conformations between a sample with MOF and a sample without MOF.

Keywords—MOF, PVDF, SEM, FIB, Raman spectroscopy, FTIR, characterization

1. INTRODUCTION

Nowadays, efforts to minimize fossil fuel use and the ever-increasing pursuit of energy self-sufficiency and renewable energy use have resulted in an increasing concentration of the scientific community developing new ways and options for harvesting energy with the least possible impact on the environment. One very promising implementation seems to be the use of a semi-crystalline polymer called polyvinylidene fluoride (PVDF), which is currently in the sights of many scientists and research institutions. The growing interest in its use lies mainly in the extent to which areas it can be implemented. It is a biocompatible, highly heat-resistant material that can be applied both in the form of thin layers and in the form of nanofibers. This ferroelectric polar polymer exhibits a high piezo-, tribo-, and pyroelectric response. PVDF has several crystalline phases differing according to their phase intermolecular conformation, which is mainly influenced by the preparation method [1, 2, 3]. The so-called metallic-organic structures (MOF) can be considered as yet unexplored and suitable for combination with PVDF. As the name suggests, this is a hybrid of organic-inorganic components consisting of metals, which is the first building block and the second block are organic linkers (otherwise also called struts or organic ligands). There is a considerable amount of their organic-inorganic structural tunability depending on the application due to their properties. Ideal use is in gas storage, sensors, filters, energy storage, or biomedicine applications [4, 5]. This is the first use of a combination of PVDF and MOF Fe(BTC). Its construction and subsequent development thus lay the basis for a completely new material, which can be used for several scientific disciplines.

2. MATERIALS AND METHODS

In this work, PVDF was synthesized in combination with iron-based MOF Fe(BTC). After the successful preparation of the solution, a flexible material in the form of nanofibers as a mat was produced. Subsequently, the investigation was carried out using several characterizations and spectroscopic methods in the form of basic research. The material was compared to the same type of material but without MOF. Both types of material (PVDF and PVDF+MOF) were created under identical conditions.
2.1. Solution preparation

Firstly, 20% polyvinylidene fluoride (Sigma Aldrich, St. Louis, USA) with molecular weight of 275,000 g/mol dissolved in dimethyl disulfide (DMDS) and acetone in a ratio of 7:3 was chosen to prepare the solution. Next, 5% iron-based MOF nanoparticles (BTC), otherwise commercially known as Basolite F300 (Sigma Aldrich, St. Louis, USA), were mixed into the solution. The resulting solution was mixed on an electric stirrer for 24 h at 80 °C and 2000 rpm. The solution was used immediately after removal from the stirrer.

2.2. Nanofiber fabrication

The resulting sample was created in the form of a nanofiber mat. Electrostatic spinning with a 4SPIN device (Brno, Czech Republic) was used for production. The spinning took place at a temperature of 24 °C and a humidity of 23%. The collector used was a rotating cylinder covered with aluminum foil and as an emitter one needle with a thickness of 17 GA, through which the solution flowed and which was subsequently drawn as a form of thin fibers due to the electrostatic forces between the emitter and collector. The flow through the needle was 35 µL/min. The high voltage between the emitter and the collector was set at 50 kV, and the speed of the collector was 2000 rpm. To better understand the whole process, the fiber was wound on a roller, like a thin thread on a spool. The resulting mat, which was applied to the aluminum foil, was then cut from the cylinder.

2.3. Characterization and observation

Several methods were used to compare PVDF and PVDF+MOF samples. As already mentioned, this is basic research aimed at determining the success of producing a combination of PVDF+MOF. Thus, electrical characterization was not included because insufficient data on the ideal structure and phase conformation of the polymer has been collected so far.

Scanning electron microscopy (SEM) provided a basic idea of the material’s structure. The observation was performed using a Lyra3 microscope (Tescan, Brno, Czech Republic) with an accelerating voltage of 5 kV. Particular attention was paid to the composition and typical morphology of PVDF and MOF. Their mutual fusion was verified. For further characterization, a focused ion beam (FIB) was used, thanks to which it was possible to observe a cross-section of the fibers. Prior to SEM observation, the samples were carbonized due to the accumulation of charge on their surface and the possibility of pure observation using the EM ACE600 coater (Leica, Wetzlar, Germany). The carbon layer had a thickness of 15 µm. Half the values are sufficient in a normal situation, but for this case—observation of nanofibers, it is necessary to apply a thicker layer, as the fibers become electrically active, and when a charge is generated on their surface, they begin to twist and move. Therefore, the thin layer would not fix them sufficiently, and the resulting SEM images would not be sharp enough.

Raman spectroscopy was used to analyze and observe the occurrence of phases during production. Thanks to this, it is possible to get an idea of a specific polarization of the sample. A green laser with a power of 5 mW was used to obtain the spectrum. The integration time was 10 s, and the spectrum was accumulated 5×. The measurement was performed with 10× objective magnification. Subsequent post-processing of the resulting spectrum consisted of background subtraction and average smoothing.

Fourier transform infrared spectroscopy (FTIR) served as a complementary method to Raman spectroscopy, which thus confirmed some of the phases occurring in the produced composite. A Vertex 80v vacuum instrument (Bruker, Billerica, USA) was used to measure the absorption spectrum with a spectral range of 4000 cm⁻¹ to 400 cm⁻¹. However, the resulting area of interest was focused on the range 1500 cm⁻¹ to 400 cm⁻¹. Baseline correction and background subtraction were done as well.

3. RESULTS

The addition of Fe(BTC) nanoparticles resulted in an expected change in the fiber structure. Not only did the nanofibers’ diameter change rapidly, but there were also swelling polymer masses in the form of beads and droplets, which were observed by SEM and cut by FIB, resulting in a different structural fingerprint and phase distribution found by Raman spectroscopy and FTIR.
3.1. Spinning and fabrication process

Due to previous experience with other additives, it was expected that problems could occur during spinning, and the resulting mat may not be firmly collected to the collector, as doped nanoparticles may affect the production process. As a reference from which all parameters were compared, the first sample without MOF was spun with already known and verified production parameters. The same setting was used for PVDF+MOF. From the course of spinning, it can be stated that the fiber mats spun smoothly and without any problems in both cases. Electrostatic spinning and production can therefore be considered successful.

3.2. Comparison of samples with and without MOF nanoparticles

After successful production, both types of samples (PVDF and PVDF+MOF) were compared. From Raman spectroscopy in Figure 1, a fingerprint of both samples can be observed, which differs considerably, especially in the proportional representation of individual bands. Upon closer examination, it is clear that the most notable difference in the ratio is achieved by the bands in the spectral region of $1524 \text{ cm}^{-1}$ and $2975 \text{ cm}^{-1}$, which indicates a different representation of materials. However, the representation of the $\alpha$- and $\beta$- crystalline phases in the region in the range of $740 \text{ cm}^{-1}$ to $880 \text{ cm}^{-1}$ is much more fascinating. The ratio of PVDF between $\alpha$- and $\beta$-phase (1:2.12) is very different to PVDF+MOF $\alpha$- and $\beta$-phase (1:1.27). It means that $\alpha$-phase ($803 \text{ cm}^{-1}$) increased almost twofold against $\beta$-phase ($840 \text{ cm}^{-1}$) for doped PVDF [6].

![Raman spectroscopy with detailed area of interest—$\alpha$- and $\beta$- crystalline phase region.](image)

**Figure 1:** Raman spectroscopy with detailed area of interest—$\alpha$- and $\beta$- crystalline phase region. Different ratios of characteristic bands can be seen over almost the entire spectrum width. However, the area where the $\alpha$- and $\beta$-phases differ between the two selected samples PVDF and PVDF+MOF is the most attractive. The different proportions of these phases can affect the electrical behavior of the sample.
Similarly, in both Raman spectroscopy and FTIR absorption regions, Figure 2 shows characteristic areas that differ significantly from pure PVDF. Thus, in addition to the different proportions between these regions in the spectrum, specific regions of the α- and β-phases can also be seen. However, in contrast to pure PVDF, the α-phase already appears strongly in the spectrum. For pure PVDF, it was not even detected at 763 cm$^{-1}$, or its value was negligible [7].

![Absorbance spectrum](image)

**Figure 2:** Comparison of two samples with and without MOF nanoparticles using Fourier transform infrared spectroscopy (FTIR). The most critical regions of the α-, β-, and γ-phases are marked. PVDF+MOF shows a strong α-phase occurrence (1383 cm$^{-1}$ and 763 cm$^{-1}$) compared to pure PVDF sample.

The pure PVDF and doped PVDF+MOF fibers are very different, as shown in Figure 3. Nevertheless, it is necessary to emphasize that the production parameters were the same for both types. The first cause that has occurred due to doped MOF is the formation of balls and drops of considerably different dimensions within units up to tens of micrometers. As seen in Figure 3b, these formations have a highly porous structure and are evaluated as imperfections of the overall composite. Ordered fibers in parallel in Figure 3a can be considered made without any issues. Another parameter that changed rapidly with the addition of MOF is the thickness of the fibers, where its difference is evident in all parts of Figure 3. An irregular, wrinkled structure can be seen upon closer examination of one fiber, especially in Figure 3c. Figure 3d shows that the imperfectly smooth structure is also visible on a thinner fiber with MOF. The fiber diameter in Figure 3c is 1018 nm and in Figure 3d is 237 nm.
Figure 3: Samples were observed on SEM and carbonated. View of the fiber structures of a) pure PVDF and b) doped PVDF+MOF. Similarly, one fiber of c) pure PVDF and d) doped PVDF+MOF is shown in detail.

3.3. Detailed surface study of MOF doped fibers

As already mentioned, the PVDF + MOF structure created in this work is new, and many interesting and specific parts should be analyzed.

One of them is created spherical objects (shown in Figure 3b too), described in Figure 4, where FIB was also used (Figure 4b). By default, these defects are called droplets, but the almost perfect spherical structure, as seen in Figure 4, pushes it to be called as balls. A cross-section of this structure (Figure 4b) revealed that some balls are hollow and porous, especially on the surface. This phenomenon has previously been observed directly on fibers [8].
4. CONCLUSION

This article describes the production and fundamental analysis of PVDF fibers with Fe(BTC) nanoparticles. The experimental findings confirmed that MOF was successfully trapped in the fibers, but
it also caused many side effects. One of them was the creation of ball structures preventing the perfect arrangement and shape of the fibers. These spherical structures are occasionally hollow. Compared to regular pure PVDF fibers, the fibers with MOF reached very low diameters. From spectroscopic measurements, PVDF+MOF showed a significantly higher α-phase than conventional fibers. These successful observations can thus serve as a basis for the further development of iron-based PVDF nanofibers. It should also be noted that this paper does not describe the specific state of iron ion binding in the composite but its importance for increasing the piezoelectric constant. For more accurate identification and fingerprint of iron, it is appropriate to use energy dispersive spectroscopy (EDX) or attenuated total reflection infrared spectroscopy (ATR-FTIR).

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