Piezoelectric properties of PVDF and PVDF-TrFE electrospun materials for nerve regeneration

F. Al Halabi[1], O. Gryshkov[1], A. I. Kuhn[1], V. M. Kapralova[2], B. Glasmacher[1]

[1]Institute for Multiphase Processes, Leibniz Universität Hannover, Callinstrasse 36, Hannover, Germany
[2]Higher School of Applied Physics and Space Technologies, Peter the Great Saint-Petersburg Polytechnic University, Polytechnicheskaja str. 29, Saint-Petersburg, Russian Federation
Contact: alhalabi@imp.uni-hannover.de, gryshkov@imp.uni-hannover.de

Introduction

Traumatic injuries and loss of functionality in peripheral nerves often lead to life-long physical restrictions. Currently, the tension-free reconstruction of longer nerve defects applying autologous nerve grafts is a gold standard in nervous tissue repair. However, the main disadvantage of this method - the complete loss of function of the donor nerve – has encouraged the scientific community to develop new tissue-engineered nerve conduits. Biosynthetic nerve guides with innovative material properties could offer alternatives to the available on the market tubular implants with very variable regeneration success. Among materials for designing of artificial nerve conduits, the ones with inherent piezoelectric properties are of high interest. Because of their proven biocompatibility, stimulation of cell ingrowth and piezoelectric properties [1, 2], polyvinylidinefluoride (PVDF) and trifluoroethylene (PVDF-TrFE) are promising materials for designing active implants for nerve regeneration. It is believed that the regeneration of severed nerves could be accelerated by these properties. The current work is based on our previous study [3] and aims to develop a measuring method to describe the electro-mechanical coupling parameter, so-called the piezoelectric module.

Materials and Methods

Preparation of materials for testing: The polyvinylidene fluoride and its copolymer polyvinylidene fluoride-co-trifluoroethylene were used as received without any purification. To prepare the polymer solutions, PVDF (Sigma-Aldrich, MW ~ 530,000 Da) and PVDF-TrFE (Piezotech Arkema, weight ratio 70/30, MW ~ 450,000 Da) were dissolved in N.-Dimethylformamide (DMF) (Fluka Analytical) and acetone (AppliChem GmbH) in a weight ratio of 6:4. For the identification of favorable conditions for production of scaffolds, the solutions with PVDF concentrations of 10%, 15% and 20% as well as PVDF-TrFE of 10%, 15% and 20% were prepared at 50 ˚C and stored at room temperature overnight prior to electrospinning.

Electrospinning of solutions: The indicated above solutions were processed by means of electrospinning to form scaffolds (fiber mats) [4, 5]. With this method, fiber mats with different polymer mass contents were produced. The focus of the selected manufacturing process was to attain the most mechanically stable fiber mats possible. For this purpose, a preliminary study of the manufacturing parameters was carried out (data not shown). In the electrospinning process, a flow rate of 2 ml/h and voltages of 20-30 kV were applied as optimal process parameters to produce aligned fibers on a rotating aluminum cylindrical collector (300 rpm). The electrospinning time for each sample was 2.5 hours.

FTIR analysis: The Fourier Transform Infrared Spectroscopy (FTIR) was used to record the infrared spectra of the electrospun scaffolds. The spectra were compared to those of untreated/raw materials with respect to the presence of the nonpolar α- and piezoelectric crystalline β-phase. The FTIR spectra were recorded using a PerkinElmer 100 FTIR spectrometer (PerkinElmer, Norwalk, CT, USA) equipped with a triglycine sulfate detector and an attenuated total reflection accessory with a diamond/ZnSe crystal. The acquisition parameters were the following: 4 cm^{-1} resolution, 8 co-added interferograms, and 4000–550 cm^{-1} wavenumber range. An automatic CO_2/H_2O vapor correction algorithm was used during recording of the spectra. Spectra analysis and display were carried out using PerkinElmer software.

Measurements using the impact press machine: The developed method is based on the direct piezoelectric effect. For this, the fiber mats were mechanically stressed using the modified impact stress machine (fig. 1) and their induced electrical value was measured.

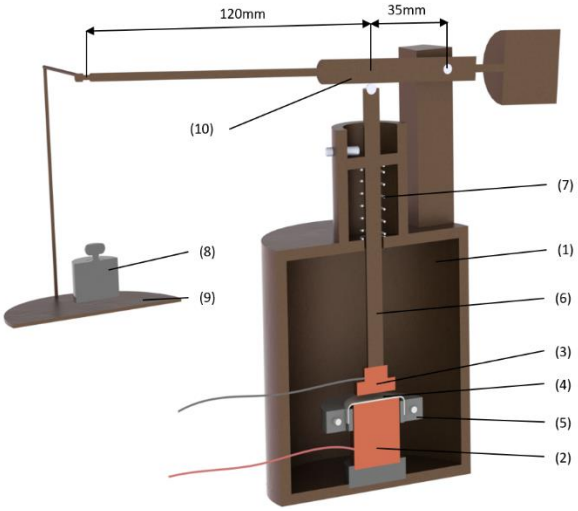

Figure 1: Section of the structure of the impact press machine: (1) measuring cell, (2, 3) electrodes, (4) test sample, (5) clamping device, (6) pressure rod, (7) spring, (8) applied weight, (9) shell, (10) lever

The measuring cell (1) is a closed shell of steel. Due to the influence in the electrical conductor, this shields the measurement against electromagnetic interference (Faraday cage). The lower electrode (2) is located in the meas-

uring cell on a polymer base which is insulated from the measuring chamber. The sample (4) is positioned in a clamping device (5) between the lower and the upper electrode (3). This consists of two rings between which the sample is clamped. The clamping device together with the sample is placed on the lower electrode, so that only the sample is in contact with the electrode surface. Due to the weight of the rings, the sample is evenly stretched over the electrode surface (fig. 2).

Figure 2: Sample without (left) and with the clamping device (right)

The upper electrode is connected to a rod (6), which projects from the measuring cell. The rod is held in position by a spring (7). On the tip of the rod there is a ball, which applies pressure uniformly to the rod and thus to the sample. The mechanical load is applied by means of a lever (10) via a weight (8), which is positioned in a shell (9). The electrodes from the measuring cell were connected to the voltage meter (610C, Keithley Instruments) during loading and unloading. The generated voltage measurement signal was then passed on to the oscilloscope (K8031, Velleman), digitized and graphically displayed on a computer via software. For capacitance measurement, the electrodes were connected to the capacitance meter (E7-20, MNIPI) in the loaded state of the sample after the voltage signal had been decayed.

The measuring principle is based on the direct piezoelectric effect. During mechanical compression of the sample, a voltage difference can be measured on the surfaces. For the determination of the piezoelectric module, the capacitance of the sample C_p must be known. Afterwards, the module d_{33} can be calculated with the following equation:

$$d_{33} = \frac{Q}{F} = \frac{w \cdot U \cdot C_p}{W \cdot F}. \qquad (1)$$

where Q: induced charge in C, F: impact force in N, U: induced voltage in V, C: electric capacitance in F, w: area of the mechanical load in cm^2, W: area of the electrodes in cm^2.

Performing measurements: The samples were fixed in the clamping device and placed on the lower electrode in the measuring cell. The measuring cell was then closed and the pressure rod adjusted so that the upper electrode did not make contact with the sample during resting. A set of weights m_{app} of 48g, 99g, 170g and 363g was used to apply the pressure load on the sample. Considering the weight of the pressure rod (m_{rod}), the upper electrode ($m_{electrode}$), the pressure compensation by the tensioning energy of the spring (m_{spring}), the conversion factor from the arm ratio of the lever (l) and the gravitational acceleration (g), the actual acting force (F_{app}) applied on the sample can be calculated as follows:

$$F_{app} = (m_{app} - m_{rod} - m_{electrode} + m_{spring}) \cdot l \cdot g = \\ = (m_{app} - 40\text{g}) \cdot \frac{120\text{mm}+35\text{mm}}{35\text{mm}} \cdot 9{,}81\,\frac{\text{m}}{\text{s}^2} \qquad (2)$$

Both the weight of the rod and the electrode as well as the pressure compensation of the spring were approximated with 40g since the contact between the upper electrode and the sample is ensured only at a weight of 40g in the shell. Tab. 1 shows the applied weights ($\boldsymbol{m_{app}}$) in the shell and the forces ($\boldsymbol{F_{app}}$) acting on the sample.

Table 1: Applied weights in the shell and the corresponding force on the sample

$\boldsymbol{m_{app}}$	48 g	99 g	170 g	363 g
$\boldsymbol{F_{app}}$	0,3 N	2,56 N	5,65 N	14,02 N

For the determination of the piezo modulus d_{33}, the voltage potentials at the surfaces and the capacitance of the samples were measured during the applied force on the sample. Fig. 3 shows the equivalent circuit diagram for the voltage measurement of the examined piezoelectric samples.

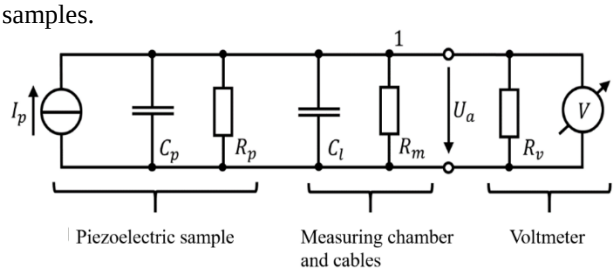

Figure 3: Electrical equivalent circuit diagram of the voltage measurement of the piezoelectric sample

In measuring the capacitance, the total capacitance (C_{tot}) has been recorded in the connected component. This included the capacitance of the sample (C_p) and the parasitic capacitance of the cables (C_l) (fig. 3). The capacitances were connected in parallel in this measurement setup. Thus, the total capacitance (C_{tot}) can be calculated using the following equation:

$$C_{tot} = C_P + C_l \qquad (3)$$

Results

Effect of polymer concentration on the crystalline β-phase: Preliminary experiments showed that 10% PVDF solution resulted in generation of fiber mats with the presence of undesired beads. For this reason, this concentration of PVDF was not taken into consideration for further investigations. The study investigated the influence of the polymer concentration on the transformation process of the crystals from α- to the piezoelectric β-phase during electrospinning.

In fig. 4, the normalized FTIR absorption spectra of electrospun fiber mats from 15% and 20% PVDF polymer solution are compared with the spectrum of raw PVDF pellet. The analysis of FTIR data demonstrates that the spectra of both fiber mats from 15% and 20% PVDF solutions do not contain peaks at 796 cm^{-1}, 976 cm^{-1} and 1383 cm^{-1} of the α-phase, as compared to the raw pellet. The characteristic peaks at 840 cm^{-1} and 1275 cm^{-1} of the β-

phase have approximately the same intensity for both fiber mats.

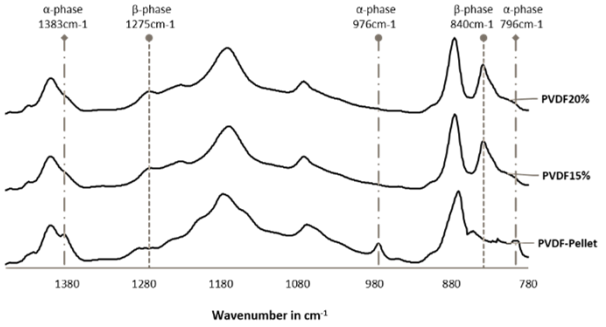

Figure 4: Normalized FTIR spectra of the raw PVDF pellet and PVDF fiber mat made of 15% and 20% polymer concentration in a DMF/acetone (6/4 ratio) solvent

Fig. 5 shows the unprocessed PVDF-TrFE powder as well as fiber mats made of 10%, 15% and 20% PVDF-TrFE solutions by means of electrospinning. In contrast to the PVDF, in which the crystals are converted into the piezoelectric β crystal phase during the electrospinning process, the PVDF-TrFE powder shows the characteristic peaks of the piezoelectric β-phase at 850 cm^{-1}, 1288 cm^{-1} und 1400 cm^{-1} [7]. Thus, the PVDF-TrFE, theoretically, does not require transformation processes for the conversion of crystallites into the β-phase. Furthermore, the three PVDF-TrFE fiber mats show nearly identical peaks at the β-phase-wavelengths.

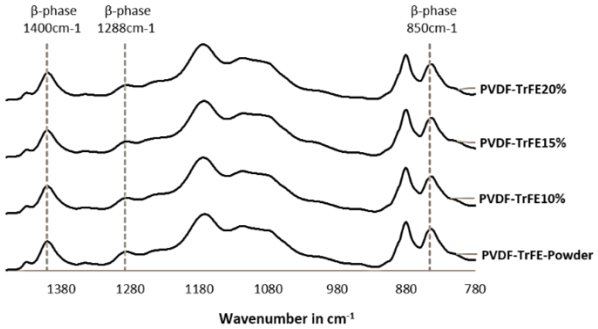

Figure 5: Normalized FTIR spectra of the raw PVDF-TrFE powder and PVDF-TrFE fiber mats made of 10%, 15% and 20% polymer concentration in a DMF/acetone (6/4 ratio) solvent

Effect of polymer concentration on the crystalline β-phase: Five fiber mats per polymer concentration were examined. Each fiber mat was manually loaded and unloaded six times, yielding 60 measuring points for each concentration. The quasi-static frequency of the measuring cycle was 0.2 Hz. Fig. 6 and 7 show measured voltages and sample capacities, respectively. Taking into account the relationship $d_{33} = (U \cdot C)/F$, fig. 8 represents the equivalent piezo modulus d_{33} of the fiber mats produced.

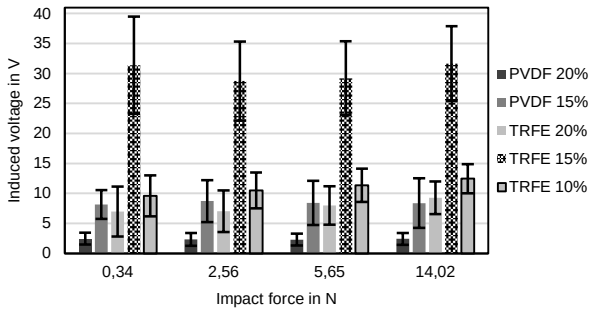

Figure 6: Measured voltages of PVDF and PVDF-TrFE fiber mats (n=6)

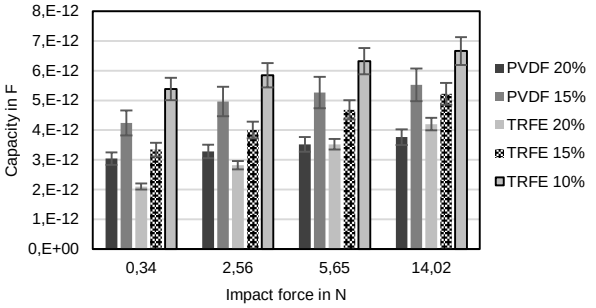

Figure 7: Measured capacities of PVDF and PVDF-TrFE fiber mats (n=6)

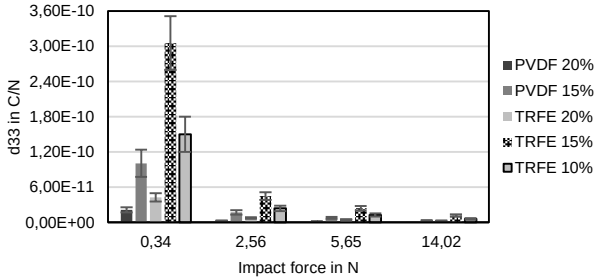

Figure 8: Piezoelectric module d_{33} of PVDF and PVDF-TrFE fiber mats (n=6).

Discussion

The piezomodule represents a geometry-independent parameter of a material, which is constant under different load profiles (by definition $d_{33} = Q/F$). If the piezomodule and the sample capacitance are known, the voltage induced at the sample surfaces during a load can be calculated with the relationship $U = (d_{33} \cdot F)/C$.

The structural transformation of α-phase into β-phase for PVDF was confirmed using FTIR analysis. This effect can be attributed to elongation of fibers during deposition onto grounded collector and simultaneous evaporation of DMF/acetone, which in turn affects orientation of dipole moments in the final PVDF electrospun fiber mat material.

For the piezoelectric investigation of the electro-spun fibrous mats from PVDF and PVDF-TrFE, an impact press machine was developed. In this method, the sample capacitance and the induced voltage were measured and then the induced charge was calculated. In order to reduce the measurement inaccuracies, the measuring charge was processed by a measuring amplifier (self-developed), taking into account the time behavior of the signal. The

measurement results showed a dependence of the piezoelectric modulus on the load, load frequency and fiber mat thickness. This behavior is due to the nonlinear viscoelasticity of the fiber mats. Since the piezoelectric modulus of the fiber mats did not behave uniformly under different load profiles, it is not possible to predict the induced voltage at a certain load.

The electrical response to a specific load profile must therefore be examined individually for different fiber mat geometries. For error-free detection of the induced voltage, a surface-covering contact between the sample surface and the measuring electrodes must be ensured. This can be performed using spinning conducting electrodes from the piezoelectric polymer and graphene oxide, as indicated elsewhere [8]. In addition, for a reproducible production of certain fiber mat geometries, a complete control of the electrospinning process has to be considered.

Conclusions

The aim of this work was to develop a measuring method to describe the electro-mechanical coupling parameter, so called piezoelectric module. The developed method is based on the direct piezoelectric effect. For this, the fiber mats were mechanically stressed and their induced electrical values were subsequently measured. In order to do this, a purely mechanical test cell for static measuring conditions was first constructed. However, the non-conductive surface structure of the fiber mats as well as the time response of the measuring signal were not considered. The measurement process on all fiber mats using the piezo module showed the same influence of the load and load frequency. As the load increased, the piezo module was reduced. Additionally, the increase in the load frequency led to an increase of the piezoelectric module. This behavior is attributed to the non-linear viscoelastic compliance of the fiber mats.

References

[1] H. Kawai. The Piezoelectricity of Poly (vinylidene Fluoride). Japan J Appl Phys, 8: 975-976, 1969.

[2] S.A.M. Tofail and J. Bauer. Electrically Active Materials for Medical Devices. World Scientific Publishing Company 2016.

[3] F. AL Halabi, L. Freund, A. Repanas, P. Behrens, S. Knigge, K. Haastert-Talini, B. Glasmacher. Effect of different solvents on morphology and properties of piezoelectric PVDF scaffolds for nerve regeneration. Biomedical Engineering, 60(S1), 2015, doi: 10.1515/bmt-2015-5000.

[4] S. Ramakrishna. An introduction to electrospinning and nanofibers. World Scientific 2005.

[5] J. Doshi and D.H. Reneker. Electrospinning process and applications of electrospun fibers. J Electrostatics, 35(2-3): 151–160, 1995.

[6] A. Szentivanyi, T. Chakradeo, H. Zernetsch, B. Glasmacher. Electrospun cellular microenvironments. Understanding controlled release and scaffold structure. Adv Drug Deliv Rev, 63(4-5): 209–220, 2011.

[7] D. Mao, B.E. Gnade and M.A. Quevedo-Lopez. Ferroelectric Properties and Polarization Switching Kinetic of Poly (vinylidene fluoride-trifluoroethylene) Copolymer. In M. Lallart, editor, Ferroelectrics - Physical Effects, chapter 4, 2011, ISBN 978-953-307-453-5, doi: 10.5772/17147.

[8] B. Li, F. Zhang, S. Guan, J. Zheng, C. Xu. Wearable piezoelectric device assembled by one-step continuous electrospinning. J Mater Chem C, 4(29): 6988–6995, 2016.

Acknowledgements

The authors acknowledge the DAAD Program Strategic Partnership with Peter the Great Saint-Petersburg Polytechnic University, Igor Katz for his excellent technical assistance as well as Prof. Dr. W.F Wolkers for assistance with FTIR experiments.

Copyright