Dielectric properties of PVDF based thin films and electrospun mats

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Abstract. Dielectric properties of polyvinylidene fluoride based thin films and electrospun mats have been studied. Frequency dependences of samples capacity and tangent of dielectric losses have been obtained. The influence of trifluoroethylene presence in copolymer on dielectric properties has been investigated. Efficiency of using deposited contacts instead of pressed contacts was considered.

1. Introduction

Polyvinylidene fluoride (PVDF) and its co-polymer with trifluoroethylene (PVDF-TrFE) have wide spectrum of applications in biomaterials. Proven piezoelectric property and biocompatibility make these polymers one of the most promising biomaterials [1] in tissue engineering and regenerative medicine. Exemplarily, they can be used to support peripheral nerve system regeneration process, especially in case of deep wounds with nerve fibre avulsions, so relevance of the study is due to the need to develop new nerve tissue implants with improved characteristics based on combined materials.

Dielectric spectroscopy is a powerful instrument of a research into molecular dynamics and relaxation processes in complex materials [2], so the main aim of this work was to characterize and compare dielectric properties of PVDF-TrFE fiber mats, PVDF and PVDF-TrFE films.

2. Materials and methods

Electrospinning is a common method for production of polymer fibers. PVDF-TrFE fiber scaffolds have been produced by using electrospinning method [3]. Polymer solutions were based on N, N-dimethylformamide (DMF) and acetone as mixed solvents. SEM photographs of the fibrous samples structure are presented in figure 1.

Before measurements, a sample of a 15% PVDF-TrFE fiber mat with deposited graphite contacts was prepared. For the deposition of contacts onto the surface of the fibrous structure, a special mixture from graphite powder with ammonia was prepared. Also, a sample of the fiber mat of 15% PVDF-TrFE without deposited contacts had been prepared which was measured using pressed contacts.

Surfaces of the films were studied using a microinterferometer. It turned out that the films consist of the micron-sized bubbles. This circumstance was the reason why the films have matte appearance. Further calculation of the dielectric constant showed that it is close to one.
Casting method was used for PVDF-TrFE and PVDF films production. Dissolving PVDF in DMF/aceton took more than 10 days at 23 °C and 1.5–3 hours at 90–100 °C. The characteristics of films are given in table 1.

| Composition       | Type of sample       | Production method   | Appearance          | Thickness (µm)          |
|-------------------|----------------------|---------------------|---------------------|-------------------------|
| PVDF              | Film                 | Casting             | Matte, opaque       | 11 ± 2 by optometer     |
| PVDF-TrFE         | Film                 | Casting             | Matte, opaque       | 10 ± 1 by optometer     |
| PVDF-TrFE with    | Fiber mat            | Electrospinning     | White porous fiber  | 150 ± 10                |
| deposited contacts|                      |                     |                     |                         |
| PVDF-TrFE with    | Fiber mat            | Electrospinning     | White porous fiber  | 140 ± 10                |
| pressed contacts  |                      |                     |                     |                         |

3. Results and discussion
A measuring cell was also designed to study the dielectric properties of the polymer films and fiber structures. At the first stage, the dependence of the sample capacity (Cp, pF) on the uniaxial pressure was measured. Loads of different masses \(m_1 < m_2 < m_3\) were placed on a special piston in the chamber to prevent surge voltage due to piezoelectric effect. The results of the experiment are presented in table 2. All experiments were carried out at a constant frequency of 1 kHz.

| Load mass       | Capacitance, pF |
|-----------------|-----------------|
|                 | PVDF film       | PVDF-TrFE fiber with deposited contacts | PVDF-TrFE film | PVDF-TrFE fiber with pressed contacts |
| 0               | 166             | 11                          | 63            | 33                        |
| \(m_1\)         | 190             | 20                          | 62            | 37                        |
| \(m_2\)         | 238             | 20                          | 59            | 41                        |
| \(m_1 + m_2\)   | —               | 21                          | —             | —                         |
| \(m_3\)         | —               | —                           | 63            | —                         |
The results given in table 2 were used to establish the measuring procedure for the fibrous and porous samples of piezoelectric polymers.

In the next step, the frequency dependence of the capacitance and tangent of the dielectric loss angle ($\tan(\delta)$) for the samples at a constant uniaxial pressure ($m_2$) was measured. After each measurement cycle, a reference measurement was performed at a frequency of 1 kHz. The measurement results are presented in figures 2–3.

**Figure 2.** A plot of capacitance ($C_p$) vs frequency.

**Figure 3.** A plot of tangent of the dielectric loss angle ($\tan(\delta)$) vs frequency.
Figure 2 evidences that the capacity of the PVDF sample significantly exceeds the values of the capacity for the PVDF-TrFE samples. Hence, the addition of TrFE substantially reduces the value of the dielectric constant.

It can be noted that value of fibrous samples capacitance is less then value for films. The reason for this decrease in the capacitance value is the presence of air pores in the fiber samples [4, 5]. Besides, capacity does not depend on frequency for all samples. The type of contacts did not demonstrate a significant impact on the value of the capacitance.

Figure 3 shows the increase of dielectric losses with frequency for all samples. In TrFE-containing samples, there is a sharp increase in dielectric losses at low frequencies, while PVDF film sample has low losses at low frequencies. This fact allows us to suppose that in TrFE-containing materials, conduction occurs at low frequencies. In addition, the use of deposited contacts improves conductivity, while the character of dependence does not change.

4. Conclusion
In conclusion, we can emphasize the following:

- the presence of TrFE in copolymer significantly reduces the value of the samples capacitance;
- the capacitance of fibrous samples is much lower than that of films due to the presence of air pores;
- TrFE-containing samples demonstrate high dielectric losses at low frequencies.

So, the combination of special dielectric and morphological properties of fibrous materials based on PVDF copolymers makes them highly prospective for tissue engineering, e.g. biocompatible artificial nerve conduits.

References
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