

# CONDUCTIVE POLYMER BASED NANOCOMPOSITE MEMBRANES FOR BIOMEDICAL APPLICATIONS

EWA STODOLAK-ZYCH<sup>1\*</sup>, MAŁGORZATA CHMIELEWSKA<sup>2</sup>,  
PIOTR JELEŃ<sup>3</sup>

<sup>1</sup> AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY,  
FACULTY OF MATERIALS SCIENCE AND CERAMICS,  
DEPARTMENT OF BIOMATERIALS,

AL. MICKIEWICZA 30, 30-059 KRAKOW, POLAND

<sup>2</sup> AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY,  
FACULTY OF ELECTRICAL ENGINEERING, AUTOMATICS,  
COMPUTER SCIENCE AND BIOMEDICAL ENGINEERING,  
AL. MICKIEWICZA 30, 30-059 KRAKOW

<sup>3</sup> AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY,  
FACULTY OF MATERIALS SCIENCE AND CERAMICS,  
DEPARTMENT OF SILICATES CHEMISTRY,  
AL. MICKIEWICZA 30, 30-059 KRAKOW

\* E-MAIL: STODOLAK@AGH.EDU.PL

## Abstract

*The aim of this work was to examine composite membranes obtained by means of phase inversion from a synthetic stable polymer – polyvinylidene difluoride (PVDF). The piezoelectric polymer was modified with 0.5-1wt% addition of commercial carbon fillers: graphite oxide (GO, 1wt%), multiwalled carbon nanotubes (CNT, 1wt%) and functionalized nanotubes (CNT-COOH, 0.5wt%). The membranes were obtained by solidification of nanocomposite solutions in coagulation bath (CH<sub>3</sub>OH). The obtained series of materials differed in surface porosity (P), electric conductivity ( $\sigma$ ) and surface free energy (SFE). It was proved that presence of carbon nanoadditive influenced microstructure of the membranes: the mean size of pores in the membrane rose in the following order: GO→CNT→CNT-COOH. The very same system depicted the influence of the filler on the membrane structure: the increase in membrane crystallinity ( $\lambda$ ) and the  $\beta$  phase share (FT Raman). From all the examined nanocomposite systems, the PVDF modified with 0.5wt% CNT-COOH displayed the most advantageous electric properties. These nanocomposite membrane (PVDF/CNT-COOH) could be used as a low-voltage electrodes in biomedical application. Yet, taking into account the other physicochemical, mechanical and structural properties, the membranes modified with 1wt% CNT and 1wt% GO were also interesting.*

**Keywords:** porous membranes, carbon fillers, polyvinylidene difluoride (PVDF), conductive, phase inversion

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## Introduction

The use of polymer conductive composites and nanocomposites based on carbon (nano)fillers (like carbon nanotube-CNT, graphite-GO, graphene-GR, carbon fiber-CNF etc.) was found to be greater in many electrical (i.e. sensors, actuators and transducers), biomedical (i.e. artificial muscles, drug release) and engineering elements (i.e. ferroelectric random access memory) [1-5]. Different form of carbon (nano)filler enhance the electrical conductivity, mechanical properties, and electromagnetic interference (EMI) shielding effectiveness of the composites [4-9]. When the carbon fillers into polymer matrix approaches the percolation threshold, the dielectric constant of composites can dramatically increase. The literature shows that direct connection between carbon fillers are a guarantee of microcapacitor network and strengthen the interfacial bonding between carbon fillers and polymer matrix [10-11]. On the other hand, the nanofiller plays a role of a nucleation center increasing an amount of crystalline structures within the polymer matrix. For this reason poly(vinylidene fluoride) (PVDF) and (nano) composites based on PVDF show advantageous properties suitable for biomedical and engineering applications [12-14]. Some of the authors reported that electrical threshold was determined by 1.2wt% MWNT into polymer matrix (PVDF) whereas the rheological percolation threshold was about 0.9-1.0wt% MWNT [15]. Chiu et al. showed that graphene sheets incorporated into PVDF/PMMA blends were characterized by good dispersion and high crystallization degree, similar to PVDF/PMMA nanocomposites modified with organoclay [16-18]. The results suggested that carbon nanofillers in PVDF have synergetic effect; their presence changes conductivity of the nanocomposite (if dispersion and nanoparticles amount guarantee to exceed the percolation threshold) and stimulates polymorphic forms (i.e.  $\alpha$ ,  $\beta$  of PVDF) which influence electrical properties of the system (PVDF/carbon nanoform). These effects are interesting for biomedical engineering particularly for biomaterials, which can be used for implants manufacturing. More and more frequently neurology and neurosurgery employ materials that facilitate nerve regeneration processes and restoration of proper nerve conductivity. In the case of peripheral nerve damage that exceeds critical loss the materials known from guided bone regeneration techniques are used [19,20]. These are usually aliphatic polyesters (PLA, PCL, PGLA and their co-polymers) of a defined degradation time. They are applied to provide the regenerating tissue with a proper environment. These materials may be scaffolds themselves (cases, tubes), facilitating the directional guidance of nerve growth, or they may fill the tissue loss (as a gel injected to improve cell growth and adhesion) [21]. Some of the biomaterials are available as implants on the medical market, e.g. Neurolac and NeuroGen.

The other group of promising materials are hydrogels. They are insoluble hydrophilic polymers with high level of swelling and cell-like mechanical properties used to fill resorbable cases or to fill the tissue loss on their own [22,23]. Chitosan, alginate, collagen and hyaluronan belong to this group. The latter material is applied in the form of a gel in microsurgical reconstructions of peripheral nerves and it is called Hyloglide [24]. Another challenging task for biomaterials application in neurosurgery is to facilitate nerve regeneration (axons) using electro-stimulation. Gordon et al. proved that short electrical stimulation with low-frequency (20 Hz for 1 h) accelerates the axon growth after the nerve cut [25,26]. It was shown that electro-stimulation modulates changes after the damage: it blocks the setback of transporting signal, resulting in acceleration of regenerative processes [27].

In other works it was also stated that during additional electro-stimulation Schwann cells increase the speed of conducting the action potential down the nerve [26]. In order to fulfil such tasks only conductive biomaterials that are both biocompatible and stable during electro-stimulation can be used [25]. Among materials that meet the requirements there are composites, nanocomposites and inert conductive materials (e.g. polyaniline PANI). Enriching the polymer matrix with a certain amount of a conductive modifier may lead to temporary or partial electric conductivity, that is why the frequent additives are carbon nanotubes (CNT). Even though their biocompatibility is a controversial issue - when closed in the matrix - CNTs may be a replacement for e.g. PANI.

The last group of materials applied in neurosurgery are substrates used for in vitro cultures of nerve cells. In these cases biomaterials must be endowed with such properties that will imitate or guarantee the environment similar to extracellular matrix (ECM) [22,28-30]. Both resorbable and inert materials (PVDF) are used here, providing they enable chemical and biological surface modifications which facilitate the growth and proliferation of nerve cells [29,30]. Based on the presented literature data, the aim of this study is to examine whether a system of an inert fluoropolymer (PVDF) modified with carbon fillers (CNT, CNT-COOH and GO) is a potential material for neurosurgical applications. A series of nanocomposite membranes were produced by means of the phase inversion method, using methanol as a coagulant. The obtained porous systems were tested to establish their mechanical, physicochemical and electric properties. The impact of nanoadditives on the structure and microstructure of the materials was also assessed.

## Materials and Methods

Commercially available polymer - polyvinylidene difluoride (PVDF) of molecular weight 80 kDa and density 1.18 g/cm<sup>3</sup> (Sigma-Aldrich) was used. The matrix modifiers were: multiwalled carbon nanotubes - CNT (NanoAmor, US) and nanotubes modified with COOH groups (NanoAmor, US). The third carbon additive used in the study was graphene oxide (Graphen Market, Germany). The properties of the materials essential for this work are presented in TABLE 1. N,N-Dimethylmethanamide (DMF, Avantor) was applied as a solvent, while methanol (CH<sub>3</sub>OH, Avantor) was used as a solidifier.

Homogenous solution of polymer PVDF:DMF (1:4) was obtained through 24-hour mixing at the temperature of 60°C at the first stage of the study. The additives were homogenized in DMF by means of ultrasounds (1 min / 20 Hz). Afterwards, the polymer was combined with the mixture and again dispersed with ultrasounds (2 min / 60 Hz). The mixture was distributed on the glass plate fixed in the device (doctor blade system).

The preliminary evaporation took place in a vacuum chamber (50°C, pressure 0.5 atm), then the substrate with the polymer film was transferred into a coagulation bath (methanol, 21°C). The thickness of the membranes was 150-180 µm. The microstructure of the membranes was observed using scanning electron microscope (Nova NanoSEM, FEI). Thanks to this technique the surface porosity and the mean size of pores were also assessed. The water contact angle (Θ) and surface free energy (SFE) were established using the goniometer DSA 10 Kruss. The electric conductivity assay was based on establishing the resistivity value of the tested membrane (Ohm's law) and dependence of resistivity (R) and electric conductivity (σ), using the universal digital multimeter (Fluke 177). The crystallinity of the materials was assessed upon the analysis of DSC curves (Netsch STA 449 F3) in the temperature range 25-600°C (protective atmosphere: nitrogen). The impact of modifying additives on the behaviour of the polymer chain was established by means of FT Raman spectroscopy (FTS 300 Excalibur, BioRad), applying the helium-neon laser of the 543.5 nm wavelength. The mechanical properties of the membranes were measured by means of tensile testing (Zwick 1435).

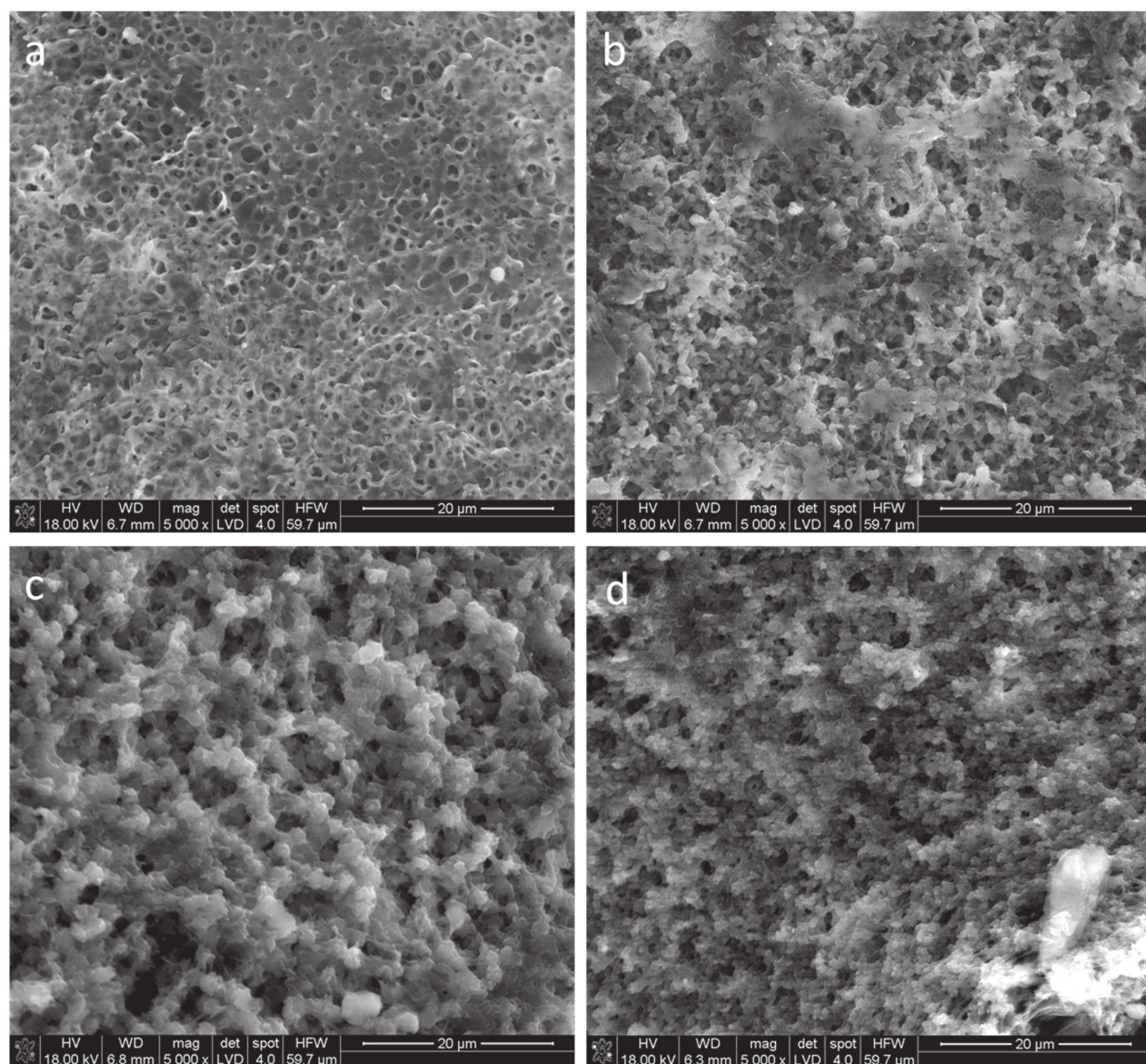
## Results and Discussions

The microstructure of polymer membranes modified with carbon nanoforms depends largely on the coagulant itself. In the literature there are reports of using other non-solvents that contribute to the process of spherulitic crystallization of semicrystal PVDF [31-33]. Methanol is a weak coagulant for PVDF, which results in its slow washing out of the solution and thus it facilitates spherulite crystallization. The size of spherulites in the tested systems also depends on the carbon nanoadditive. Graphene oxide flakes (GO) impede formation of spherulites (they reduce chain mobility, FIG. 1b). In SEM images a higher number of tiny spherulites is observed in comparison to the polymer membrane (PVDF, FIG. 1a). In turn, addition of CNT promotes formation of crystallites (FIG. 1c-d). Nanotubes, particularly the surface-modified ones, make heterogenic seeds of crystallization. It makes spherulites bigger and less numerous (FIG. 1). On all the membrane surfaces the characteristic network of interconnected spherulites is observed. The estimated size of surface pores in the tested membranes decreases in the following order: 1wt% GO (max. diameter up to 2.5 µm) → 0.5wt% CNT (max. diameter up to 6 µm) → 1wt% CNT-COOH (to 8 µm). Having analysed the porosity results obtained by means of a bubble point method, it was stated that the highest porosity characterizes two kinds of the examined membranes: the nanocomposite membranes with 0.5wt% of CNT (approx. 52%) and the membranes with 1wt% of CNT-COOH (48%). In reference to the literature data they are porosity values suitable for neurosurgical applications – they promote selective transfer of cells and nutrients [20,22,34].

**TABLE 1. Key properties of nanoadditives as provided by manufacturers.**

Material	Producer	Morphology	Tensile strength [GPa]	Electric conductivity [S/m]
GO	Graphen Market Co	flake thickness 60 nm flake size 3-7 µm	130	7200
CNT	NanoAmor, US	diameter 1-5 nm length 1 µm	60-150	3000-4000
CNT-COOH	NanoAmor, US	diameter 3-10 nm length 2 µm	50-80	3500-4500





**FIG. 1. Microstructure of membranes based on PVDF modified with carbon nanofillers: 0.5wt% CNT (c), 1wt% CNT-COOH (b), 1wt% GO (d). Reference membrane with neat PVDF (a).**

Crystallinity of the membrane materials was determined in the first place by the precipitating agent – methanol. The analysis of DSC curves confirms that typical effects i.e. melting point of the crystalline phase ( $T_m$ ) is exothermic, unlike in the case of membranes precipitated with e.g. water. This effect may be explained by the reorganization of the chains to improve their order. Another factor affecting the size of spherulites is the type of carbon filler. CNT initiates the formation of spherulites, that is why the crystalline phase share increases (TABLE 2). The bigger size of the filler (CNT-COOH, GO) is, the more slowly crystallinity increases. In the case of PVDF/CNT-COOH membrane, the essential factor is the amount of the filler twice as big as in the case of CNT. During the precipitation polymer chains form lamellas and/or spherulites (observed by SEM).

**TABLE 2. Thermal properties of membrane nanocomposite system PVDF/carbon nanoform and the pure polymer membrane (reference).**

	PVDF membrane	PVDF/CNT membrane	PVDF/CNT-COOH membrane	PVDF/GO membrane
$\Delta H$ [J/g]	60.6	62.8	58.7	46.5
$\lambda$ [%]	57.9	60.1	55.8	44.2
$T_m$ [°C]	165.0	165.0	165.0	157.5
$T_r$ [°C]	474.0	476.0	478.0	460.0

Modification of the pure PVDF leads to lowering the surface free energy (SFE) and components  $\gamma_p$  and  $\gamma_d$  in relation to the unmodified polymer PVDF (SFE = 30.3 mJ/m<sup>2</sup> when  $\gamma_d$  = 23.3 mJ/m<sup>2</sup> and  $\gamma_p$  = 7 mJ/m<sup>2</sup>) [35]. Graphite oxide lowers the surface free energy of the membrane, while sustaining its hydrophobic character (the  $\gamma_d$  value bigger than  $\gamma_p$ ). It is not a surprising phenomenon: a slight amount of hydrophilic filler exposes the polar groups on the membrane surface. In turn, carbon nanotubes significantly raise the SFE value (for CNT it is 35 mJ/m<sup>2</sup>, for CNT-COOH it is 53.5 mJ/m<sup>2</sup>). In both cases (PVDF/CNT and PVDF/CNT-COOH) the material remains highly hydrophobic (FIG. 2a). It seems that carbon nanotubes during the solidification process are surrounded with polymer chains (thus bigger spherulites are observed), that is why fluoropolymer groups get exposed on the membrane surface (thus SEM similar to pure PVDF). The wettability results indicate that GO-modified membranes do not differ from pure polymer membranes, contrary to the membranes modified with nanotubes. In their case the 15% increase in hydrophobicity is noted (FIG. 2b). Physicochemical properties of the surface confirm potential applications of the materials for GNR (especially PVDF/GR membranes). The materials may be also used as coatings for electrodes in electro-stimulation (PVDF/CNT, PVDF/CNT-COOH) [25,36]. Also the values of electric conductivity confirm the possibilities of the materials in question. The membranes with CNT addition endowed with well-developed spherulitic microstructure display higher conductivity (approx. 28300-32800 [S]). Electric conduction in nanocomposite systems with carbon additive is based on so-called "hopping" in lamellar or spherulitic structures, provided that the nanoadditive is distributed homogeneously [37]. It seems that during the membrane precipitation the more numerous phase  $\beta$ -PVDF with increased electric conductivity is formed [38,39]. The microstructure with higher crystallinity and better-organized order of PVDF chains enriched with a conductive addition provides more conductive paths.

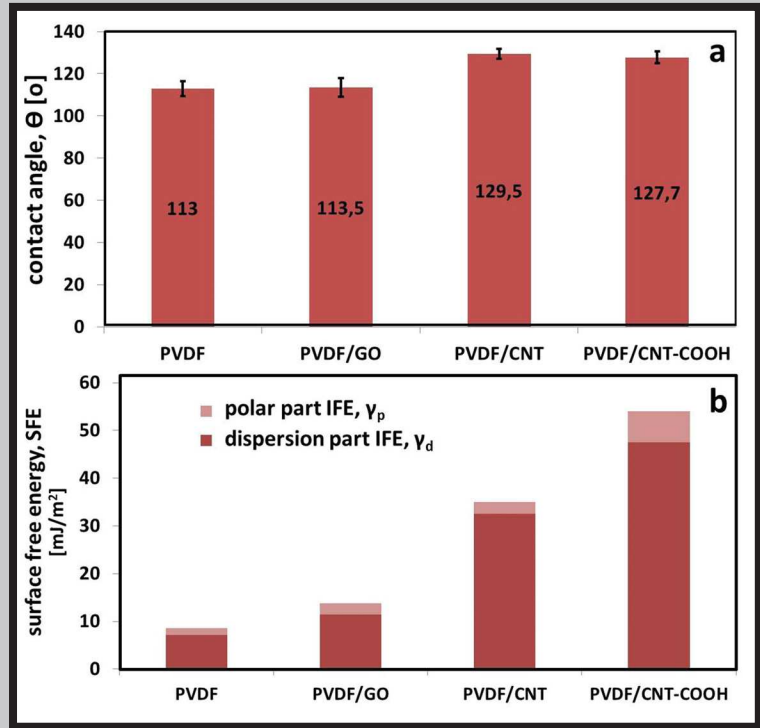


FIG. 2. Physicochemical properties of surface of membrane with carbon nanofiller: water contact angle (a), surface free energy (b).

The Raman spectroscopy analysis showed that in the spectrum of PVDF membranes there are bands characteristic for  $\alpha$ ,  $\beta$  and  $\gamma$  phases (FIG. 3). The  $\alpha$  phase may be present either on its own (it is confirmed by the bands at 615 cm<sup>-1</sup>, 795 cm<sup>-1</sup>) or as a mixture of  $\alpha$  and  $\beta$  phases (at 880 cm<sup>-1</sup>) or as  $\alpha$ ,  $\beta$  and  $\gamma$  mixture (at 1130 cm<sup>-1</sup>). The other characteristic bands may be assigned to the  $\gamma$  phase (810 cm<sup>-1</sup>) or the  $\beta$  and  $\gamma$  mixture (840 cm<sup>-1</sup>) [40]. The application of modifiers diminishes the share of the  $\alpha$  and  $\gamma$  phases, while the phase  $\beta$  share increases. Additionally, in the spectrum of membranes with carbon additives there are bands typical for carbon structures i.e. CNT and GO: D band (at 1340 cm<sup>-1</sup>), G band (at 1580 cm<sup>-1</sup>) and G' band (at 2680 cm<sup>-1</sup>) [18, 41].

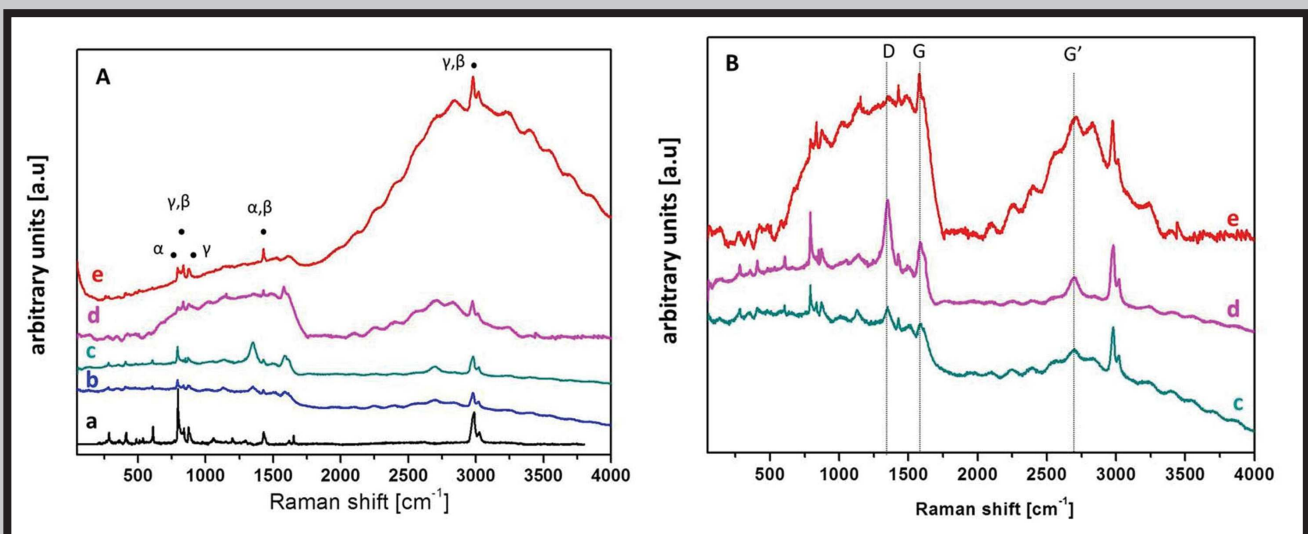


FIG. 3. Raman spectra of various type of materials: neat PVDF pallets (a), reference membrane base on PVDF (e), polymer membrane modified by carbon nanofiller: 0.5wt% CNT (b), 1wt% CNT-COOH (c), 1wt% GO (d).



**TABLE 3. Mechanical properties of nanocomposite membrane based on PVDF.**

	PVDF membrane	PVDF/CNT membrane	PVDF/CNT-COOH membrane	PVDF/GO membrane
Young's modulus E [MPa]	187.8 ±2.5	54.3 ±1.2	36.7 ±0.5	164.8 ±1.9
Mechanical strenght $R_M$ [MPa]	2.41 ±0.12	1.27 ±0.18	3.17 ±0.19	10.28 ±0.5
Conductivity $\sigma$ [S]	10 <sup>-6</sup>	32800	28300	18400

The lack of the D band in PVDF/GO membrane is caused by the absence of disordering that results from the sp<sup>3</sup> hybridization which is not present in graphite (there is only sp<sup>2</sup>). Comparing the intensity of bands D and G for membranes with carbon additives the better interaction between the carbon filler and the polymer chain is expected for PVDF/CNT and PVDF/CNT-COOH ( $I_D/I_G > 1.1$ ). The opportunity to create interactions between  $\pi$  electrons and fluorine electrons from the PVDF chain takes place already during the membrane formation (precipitation with methanol). Thus the obtained membrane is a more stable system with a higher degree of crystallinity and increased electric conductivity.

Unfortunately, the carbon additive of CNT negatively affects the mechanical properties of the membranes (TABLE 3). It significantly decreases the Young's modulus (E) value and the tensile strength ( $R_M$ ), as compared to the membrane made of pure polymer. It is not a surprising result when confronted with the increased surface porosity of polymer-carbon membranes. However, this parameter does not play a key role in medical applications – neither implants for peripheral nerve regeneration nor coatings modifying the surfaces of electrodes require higher values of E or  $R_M$ .

## Conclusions

The method applied makes it possible to manufacture the PVDF-based membranes with homogeneous microstructures. The time it takes methanol to wash out the solvent enables the formation of interconnected spherulites. These forms are characterized by high crystallinity and strong conductive phase  $\beta$  PVDF. The addition of carbon nanoparticles and crystallization from the solution also increases the amount of the phase  $\beta$ . All the examined nanocomposite systems display conductive properties. The effect depends on a kind of nanoadditives. It was shown that a flaked filler (GO) displays the least electric conductivity, low crystallinity and surface porosity, while sustaining the surface wettability and energy on the level comparable to the properties of a pure membrane. It results from the behaviour of a polymer chain in contact with a flake of graphite. Such a form significantly limits the mobility of polymer chains, impeding crystallinity and destabilizing the membrane morphology (lack of effective connections between spherulites, thus low mechanical properties). In turn, nanotube filler increases the values of electrical conductivity, surface porosity and size of pores. Also the hydrophobicity of the membranes increases distinctly, which will probably hinder the adhesion and proliferation of cells. Thereby, the PVDF membranes modified with CNT are better coatings for low-voltage electrodes, due to their stability of microstructure, high electric conductivity and low wettability.

To sum up, the use of methanol and a selected carbon modifier may result in a synergic effect connected with improvement of structural, electrical and surface properties of the materials, which will make them more suitable for neurosurgical applications.

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