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A R T I C L E I N F O

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A B S T R A C T

Conducting macroporous soft cryogels were prepared by the oxidation of pyrrole within the frozen aqueous solutions of 5-8 wt.% poly(vinyl alcohol) at — 24 °C. Mechanical properties of cryogels were independent of poly (vinyl alcohol) concentration, Young moduli were ≈20 kPa. The conductivity of compressed freeze-dried composites reached 18 S cm^{-1} thus exceeding the conductivity of polypyrrole alone. This level of conductivity was also preserved after long-term treatment with water, *i.e.* close to physiological conditions. *In-vitro* determined cytotoxicity demonstrated high potential applications due to low cytotoxicity. Moreover, compared to the steel based materials, the cryogels mimic the properties of soft tissues. All these properties are a prerequisite for the utilization in biomedical applications.

1. Introduction

Polypyrrole (PPy) is a conducting polymer which possesses unique chemical and physical properties, such as high electrical conductivity, redox properties, environmental stability, ease of preparation and biocompatibility [**1-3**]. These particular properties enable PPy to be used in widely differing applications, such as in supercapacitors [**4-6**], batteries [**7,8**], sensors [**9-11**], as adsorbents [**12,13**], electroactive separation membranes [**14**], anti-corrosion coatings [**15,16**], and others. In recent years, however, PPy has attracted great attention as a functional material in biological and biomedical applications, including cardiac and neural-tissue engineering [**17-19**], drug delivery [**20,19**], and biosensors [**21,22**]. Due to its poor processability, owing to the insolubility and infusibility, the use in practical applications is limited and various composite forms have been sought to overcome this problem [**4,5,7,12,23**], *viz.* colloids [**24,25**] and hydrogels [**18,26**].

The last form, conducting hydrogels, became the most prospective material in biomedicine due to their soft texture, biocompatibility, mixed electron and proton conductivity and good mechanical properties [**27**]. Conducting polymer hydrogels can be obtained in two basic ways [**26**]: (1) by the preparation of conducting polymer within hydrogel matrix [**10,17**], or (2) by the preparation of hydrogels in the presence of a conducting polymer [**28**]. The former approach dominates in the literature. The resulting hydrogels, however, suffer usually from uneven distribution of conducting polymer phase.

New class of conducting polyaniline materials, cryogels, have recently been developed [**29-33**]. Unlike the current approaches, the conducting polymer and supporting hydrogel phase have been produced in a single step. The polymerization of aniline was conducted in the presence of water-soluble polymer, poly(vinyl alcohol) (PVAL), in a frozen reaction mixture and cryogels were obtained after thawing [**29**]. Composite polyaniline/PVAL cryogels are three-dimensional, macroporous, conducting polymeric networks combining electrical properties of polyaniline with mechanical properties of PVAL-based cryogels. The term "cryogel" refers to the way of preparation [**34**]; a "hydrogel" is the final product.

In the present work, the facile, one-step procedure of the preparation of multifunctional macroporous conducting hydrogel was extended to polypyrrole/poly(vinyl alcohol) (PPy/PVAL) (**Fig. 1**). The resulting composite cryogels are macroscopically homogeneous and possess high electrical conductivity, which is preserved even upon deprotonation in water under physiological conditions. In addition, their biocompatibility has been investigated with the promising result.

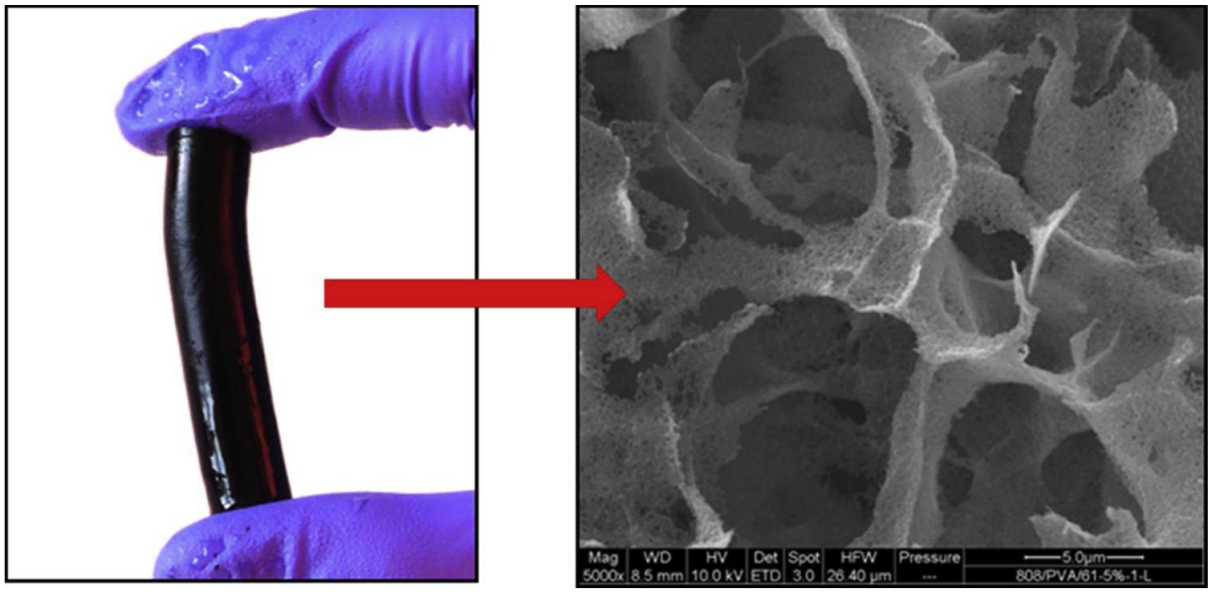

Fig. 1. Composite polypyrrole/poly(vinyl alcohol) cryogel prepared with 5wt% of poly(vinyl alcohol) (left) and illustration of macroporous morphology of corresponding aerogel (right).

2. Experimental

2.1. Preparation

Polypyrrole/poly(vinyl alcohol) cryogels were prepared by the oxidation of pyrrole (0.2 M; Sigma-Aldrich) with iron(III) chloride hexahydrate (0.5 M; Sigma-Aldrich) in the presence of various concentrations, 5-8 wt%, of poly(vinyl alcohol) (Mowiol* 10-98, molecular weight 61,000; Sigma-Aldrich) in water. The fresh mixture of pyrrole and oxidant in poly(vinyl alcohol) solutions was quickly sucked into a plastic syringe, frozen in solid carbon dioxide/ethanol suspension at — 78 °C, and then left in a freezer at — 24 °C for 7 days to allow pyrrole to polymerize. After thawing at room temperature, cryogels were removed from syringe and immersed in excess of water or 0.2 M hydrochloric acid to extract any residual reactants and by-products. The corresponding PPy/PVAL aerogel was obtained by freeze-drying of cryogels.

2.2. Characterization

Morphology of freeze-dried PPy/PVAL cryogels was studied by scanning electron microscope (SEM) Vega Plus TS 5135. Static mechanical properties of hydrogels were analyzed on electromechanical testing device Instron 6025/5800R equipped with a 10 N load cell at room temperature and with a cross-head speed of 10 mm min^{-1}. Cylindrical specimens with diameter 3 mm and length 60 mm were employed in the environment of deionized water. At least 3 measurements had been performed and the results were averaged.

DC electrical conductivity was obtained by a van der Pauw method on dried cryogels compressed to pellets (diameter 13 mm, thickness = 1 mm) at 530 MPa using a hydraulic press Trystom H-62. A Keithley 230 Programmable Voltage Source in serial connection with a Keithley 196 System DMM served as a current source, the potential difference between the potential probes was measured with a Keithley 617 Programmable Electrometer. The conductivity was obtained as an average value from the measurements in two perpendicular directions at room temperature 23 °C and relative humidity 35 ± 5%.

The specific surface area of the samples was determined by Brunauer-Emmett-Teller (BET) method using a Gemini VII 2390 (Micromiretics, Instruments Corp, Norcross, USA) with nitrogen as the sorbate. The samples were vacuum-dried at 130 °C for 50 h.

The cytotoxicity was assessed by the procedure reported earlier [**3,30**]. In brief, the Mouse embryonic fibroblast cell line (ATCC CRL- 1658 NIH/3T3, USA) was used for testing according to the ISO 10-9935 and 10-993-12 standards. The cell viability was determined using colorimetric MTT assay. MTT cell-proliferation assay is a colorimetric reaction based on the reduction of a tetrazolium component (MTT; 3- [4,5-dimethylthiazole-2-yl]-2,5-diphenyltetrazolium bromide) into an insoluble formazan product by the mitochondria of viable cells.

3. **Results and discussion**

3.1. Cryogel characterization

Polypyrrole is usually prepared by the polymerization of pyrrole with iron(III) chloride [**10,35,36**]. When the same polymerization is carried out in aqueous medium in the presence of PVAL in the frozen state, *i.e.* in ice, black PPy/PVAL cryogels are obtained (**Fig. 1**). Elemental analysis of freeze-dried cryogel revealed that they contain from 41 to 49wt.% of PPy for various amount of PVAL used for their synthesis. Scanning electron microscopy images revealed that cryogels have an interconnected, uniform, three-dimensional macroporous network with macropore diameters from 5 to 100 pm (**Fig. 2**). It can be observed that pore size does not depend on the concentration of PVAL used for the preparation of cryogels. Similar pore size was observed previously when the same preparation technique was applied to poly- aniline/poly(vinyl alcohol) cryogels [**29**]. This confirmed the hypothesis that pore size in cryogels is given by the size of ice crystals formed during the freezing of the polymerization mixture [**29**]. The pore walls are microporous and seem to be composed of globules of PPy incorporated in ultra-thin layer of PVAL matrix (**Fig. 1**). However, the specific surface area of PPy/PVAL cryogel is rather low, from 0.45 to 14 m^2g^{-1} (**Table 1**) and only slightly changes with amount of PVAL.

Various concentrations of poly(vinyl alcohol) do not have influence on the stiffness of the PPy/PVAL cryogel (**Table 1**), so the mechanical properties are controlled by PPy phase. Despite a low Young modulus, = 20 kPa, these soft and macroporous cryogels are easy to handle and manipulate (**Fig. 1**).

The conductivity of PPy/PVAL cryogel was analyzed on pressed pellets from freeze-dried material before and after deprotonation with water (**Table 1**). The conductivity of protonated composite cryogel is = 18 S cm^{-1}, which is higher than neat PPy prepared by oxidation of pyrrole with iron(III) chloride (units S cm^{-1}) [**37**]. This is explained by different PPy chain organization in various morphologies [**38**]. Similar polymerization of aniline in the presence of PVAL in frozen state, however, led to polyaniline/PVAL cryogel with conductivity much lower than that of corresponding polyaniline [**29**]. When the composite materials of PPy with non-conducting component are prepared, the conductivity is usually expected to decrease by a few orders of magnitude (**Table 2**). The fact that their conductivity maintained at the same level after extensive washing of such cryogels with water for 3 months makes PPy in general [**39**] and PPy/PVAL cryogel in particular promising materials for potential biomedical applications.

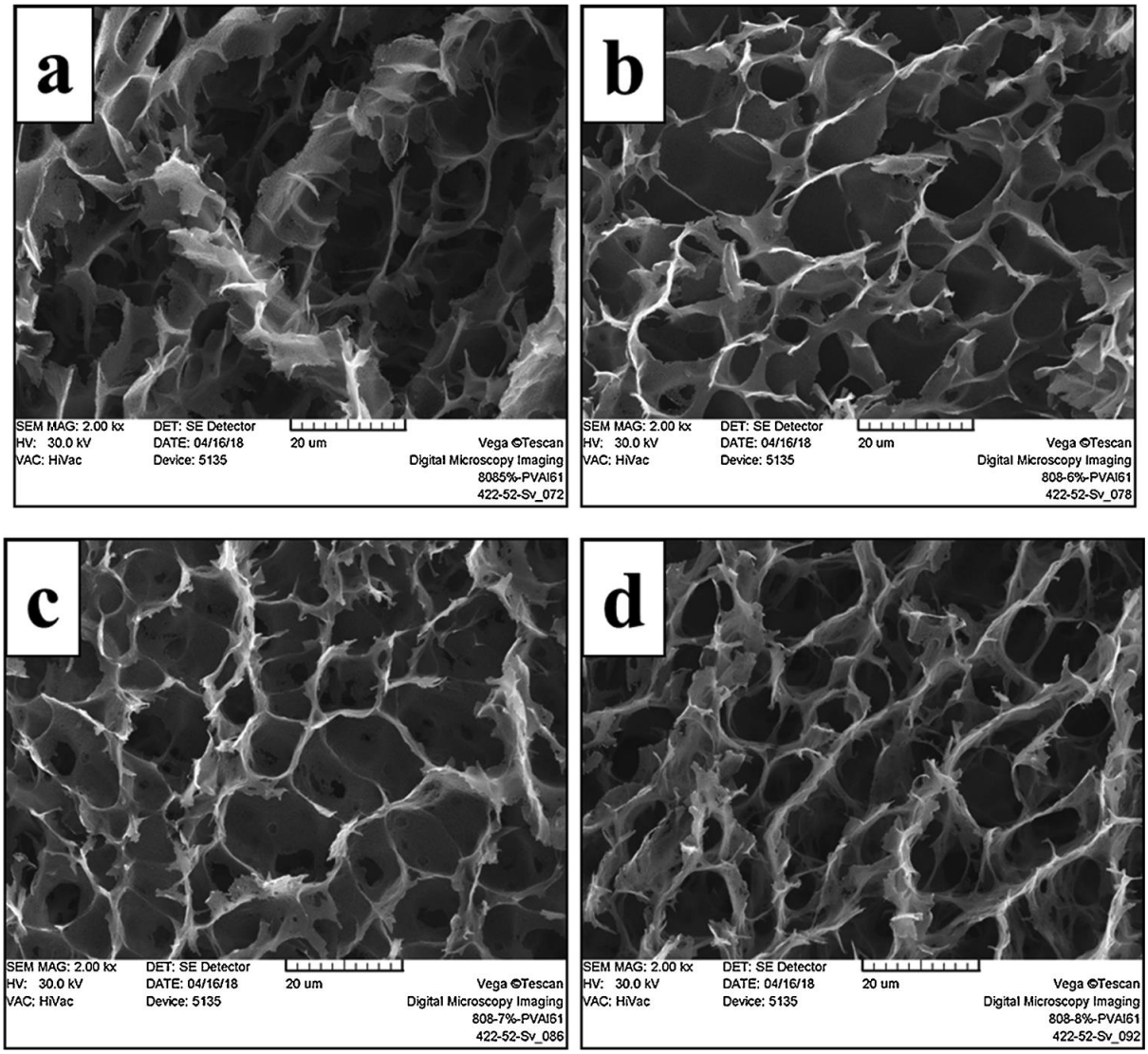

Fig. 2. Scanning electron micrographs of freeze-dried polypyrrole/poly(vinyl alcohol) cryogels prepared in the presence of (a) 5, (b) 6, (c) 7 and (d) 8 wt% of poly (vinyl alcohol).

Table 1 Mechanical properties of polypyrrole/poly(vinyl alcohol) cryogels, and conductivity and surface area of corresponding freeze-dried material.

Poly(vinyl alcohol) concentration, wt%	Young modulus (kPa)	Tensile strength (kPa)	Tensile strain at break (%)	Conductivity (cryogels washed with acid) (S cm^{-1})	Conductivity (cryogels washed with water) (S cm^{-1})	BET surface area (m^2g^{-1})
5	18.8 ± 3.0	1.5 ± 0.1	9.3 ± 0.1	14.8	6.1	0.45
6	22.1 ± 0.9	2.0 ± 0.2	9.9 ± 0.2	18.4	6.8	14.1
7	22.8 ± 2.8	2.4 ± 0.5	13.0 ± 0.5	12.9	7.1	11.1
8	16.2 ± 2.1	2.4 ± 0.4	15.0 ± 0.4	8.2	7.4	3.4

Table 2 Conductivity, o, and biological properties or intended application of polypyrrole and its composite hydrogels and cryogels.

Polypyrrole/hydrogel support	σ (S cm^{-1})	Biological properties	Ref.
Globular polypyrrole reference	0.3	–	[37]
Alginate	1×10^{-4}	*In vitro* – supported human mesenchymal stem cells attachment and proliferation	[17]
Poly(amino ester)	6×10^{-4}	*In vivo* – efficiently promoted the cardiac function and enhanced the conduction of electrophysiological signal and revascularization of the infarct myocardium	[18]
Chitosan/polyacrylic acid/magnetite	1.9×10^{-4}	–	[40]
Sodium alginate/carboxymethylchitosan	8×10^{-3}	*In vitro* – rat adrenal pheochromocytoma cells (PC12), Schwann cell lines (RSC96) and bone marrow mesenchymal stem cells exhibited good adhesion and proliferation *In vivo* – without inflammatory reaction after 5 weeks and can be support for peripheral nerve regeneration	[41]
Polyacrylamide (cryogel)	1.5×10^{-4}	–	[42]
	–	*In vitro* – Human hepatoma derived cell line (HepG2) and rat glial cells (C6) indicated good biocompatibility	[43]
Poly(acrylic acid) (cryogel)	3.5×10^{-4}	–	[42]
Poly(4-vinylpyridine) (cryogel)	2.5×10^{-4}	–	[42]
Chitosan	–	*In vitro* – neonatal cardiomyocyte exhibited good adhesion and proliferation *In vivo* – can improve electrical conduction across a fibrotic scar in the injured heart	[44]

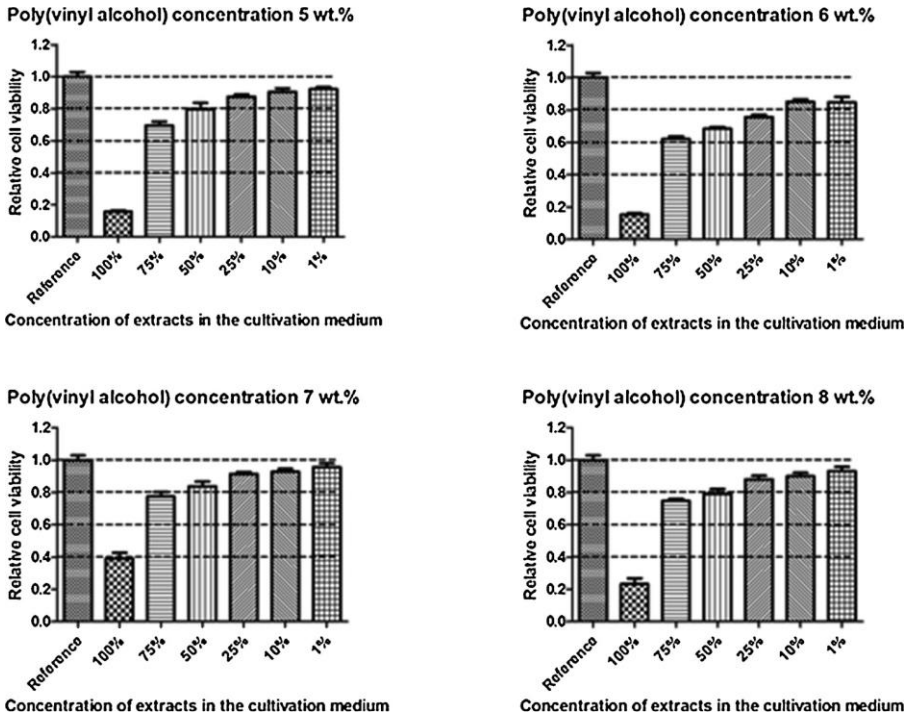

Fig. 3. Cytotoxicity of extracts of PPy/PVAL cryogels towards NIH/3T3 cells determined by MTT assay. The dashed lines highlight the limits of viability according to EN ISO 10993-5 where viability > 0.8 means no cytotoxicity, 0.6-0.8 mild cytotoxicity, 0.4-0.6 moderate toxicity, < 0.4 severe cytotoxicity.

3.2. Cytotoxicity

Considering the cytotoxicity of PPy/PVAL cryogels, the only moderate correlation of cytotoxicity to the different concentrations of PVAL was found (**Fig. 3**). In fact, the cytotoxicity of PPy/PVAL cryogel was observed only in the case of 100% concentration of extracts in cultivation medium. Adverse effect of 100% extracts is moreover connected to the change of acidity of cultivation medium due to releasing of residual acids from preparation procedure of cryogels (the testing was performed on native samples, without any additional purification). In the case of any application, the determined low cytotoxicity can be regarded as negligible because for lower concentration of extract the cytotoxicity is eliminated, especially for 7 and 8wt% of PVAL in cryogel.

PVAL is generally considered as biocompatible material, thus the observed slight impact of extracts of PPy/PVAL cryogels on cell viability can be connected mainly to the presence of PPy. According to the study of Humpolicek et al. [**3**], the cytotoxicity as well as the embry- otoxicity of PPy is closely connected to its form, salt vs base, and it is associated with the presence of low-molecular-weight impurities and not to the polymer itself. Observed biological properties of PPy/PVAL correspond to the generally good biocompatibility of PPy-based hydrogels (**Table 2**). There are, moreover, the studies demonstrating the superior properties of PPy-based materials towards the use in electro-sensitive tissues, *e.g.,* cardiac patches [**18**]. The porous cryogels are thus promising for application as bio-interfaces.

4. Conclusions

The soft macroporous conducting cryogels were prepared by a single-step polymerization of pyrrole in the frozen aqueous solutions of poly(vinyl alcohol). Compressed freeze-dried composites have conductivity exceeding the conductivity of standard polypyrrole alone and the conductivity is maintained even when cryogels was washed with water (pH close to physiological conditions). The cryogels are soft with good mechanical properties and biocompatibility sufficient to make them suitable for potential biomedical applications.

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