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Electrophysical properties of chitosan-based composite films filled with single-wall carbon nanotubes

A. M. Kamalov✉[1], V. V. Kodolova-Chukhontseva[1], E. M. Ivan'kova[2], M. E. Borisova[1], V. E. Yudin[2]

[1] Peter the Great St. Petersburg Polytechnic University, 29 Polytechnicheskaya Str., Saint Petersburg 195251, Russia
[2] Institute of Macromolecular Compounds RAS, 31 Bolshoy Ave., Saint Petersburg 199004, Russia

Authors

Almaz M. Kamalov, ORCID: 0000-0003-2044-957X, e-mail: spb.kamalov@gmail.com

Vera V. Kodolova-Chukhontseva, ORCID: 0000-0001-8314-5317, e-mail: vera_kodolova@mail.ru

Elena M. Ivan'kova, ORCID: 0000-0002-4823-0695, e-mail: ivelen@mail.ru

Margarita E. Borisova, ORCID: 0000-0003-0761-6302, e-mail: vladimirl.borisov@gmail.com

Vladimir E. Yudin, ORCID: 0000-0002-5517-4767, e-mail: yudin@hq.macro.ru

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Abstract. This work focuses on new chitosan-based composite materials. In order to improve chitosan conductivity, single-wall carbon nanotubes (SWCNT) were added as a filler. The structure of the composites was studied using a scanning electron microscope. It is shown that the addition of SWNCT filler leads to chitosan structure ordering. The increase in SWCNT content from 0 wt.% to 3.0 wt.% leads to an increase in composite film conductivity from 10^{-11} to 10 S/m, with the relative dielectric permittivity change from 5.5 to 26 at 1 kHz. The effect of moisture on the films' dielectric properties was also studied.

Keywords: chitosan, nanotube, conductivity, dielectric properties, percolation threshold

Introduction

In recent years, polymer materials have been widely used in cell technology, regenerative medicine, or as a part of devices for open wound treatment. For these materials to be used in such applications, they do not only need an approval for medical use, but should also have suitable properties ensuring their bioactivity. In order to achieve this, the structure of a material needs to be as similar to the structure of a living tissue as possible (Vladkova 2010). One of the most effective cell regulation technologies is the use of electrical stimulation through conducting materials (Liu et al. 2021).

Single wall carbon nanotubes (SWCNT) are a promising filler for composite materials, which can significantly alter the initial electrophysical properties of a polymer film. SWCNT are used as drug carriers (Chen et al. 2008; Cheng et al. 2011; Pan et al. 2009), biosensors and composite matrices in cell technology (Abarrategi et al. 2008; Guo, Ma 2018; Mitrofanova et al. 2014). They have recently been used as a conductive filler in composite materials (Matrenichev et al. 2018) and in stem cell growth projects (Lorite et al. 2019; Lovat et al. 2005).

Chitosan is one of the most promising polimers for medical use in dermal regeneration technologies. Made from chitin, chitosan has a full range of biological properties, such as biocompatibility, bioactivity

and bioresorbability (Kumar 2000). Although chitosan-based materials possess useful medicinal properties, their conductivity is generally insufficient. Electrical signals are involved in various biological processes, such as cell communication and tissue regeneration. Therefore, tissue engineering matrices need a certain level of electrical conductivity to increase their biocompatibility, stimulate cell processes and facilitate cell adhesion, proliferation and differentiation (Stewart et al. 2015; Yang et al. 2016).

The addition of SWCNT (up to 10 m%) leads to an increase in the conductivity of a material and improves its mechanical properties (Huang 2020; Matrenichev et al. 2018). A low concentration of SWCNT makes it possible to minimise potential polymer cytotoxicity.

The goal of this work was to develop new conductive chitosan-based composites and to study the effect of SWCNT addition on the composites' electrophysical properties.

Materials and methods

The composite films were obtained from the mixture of SWCNT and 4% solution of chitosan in 2% acetic acid. The samples were made from shrimp chitosan (CS) manufactured by Biolog Heppe GmbH (Germany) with a molecular mass of $1.64 \times 10^5 – 2 \times 10^5$ and deacetylation degree of 92.4%. Single wall carbon nanotubes were purchased from Carbon Chg, Russia. The average diameter of SWCNT was equal to 1.4 ± 0.3 nm; their length was 1–5 μm. An aqueous dispersion containing SWCNT was subjected to ultrasound treatment using an IL10–0.63 ultrasonic bath for 15 min (25 kHz, 630 W). Chitosan was introduced into the SWCNT aqueous dispersion in the amount resulting in polymer concentration of 4.0% and the required chitosan/SWCNT ratio.

The mixture of chitosan and SWCNT in water was stirred for 30 min in order to achieve chitosan swelling and partial dissolving. After that, acetic acid was added to the mixture (2% concentration). The solution was stirred for 180 min, filtered and deaerated in a vacuum chamber for 24 h at a pressure of 10 kPa. SWCNT contents were 0.1, 0.5, 1.0 and 3.0 wt.%. The films were prepared by extruding the solution onto glass substrate through a slit die. Subsequently, the films were dried at 50 °C for 1 h. The films on a glass substrate were deaerated in a vacuum chamber at 10 kPa and dried in air at room temperature (24 h each). The obtained films were exposed to 10% aqueous solution containing NaOH and C2H5OH (1:1) for 10 min, then they were washed with distilled water and dried in air (Fig. 1). The film thickness was 30 ± 5 μm.

Fig. 1. Optical images of chitosan-based films containing 0.0.5, and 3 wt.% of SWCNT (a, b, c, respectively)

The structure of nanocomposite chitosan films was studied with electron microscopy, using SUPRA-55VP instrument (Carl Zeiss, Germany).

The electrical conductivity of the samples was measured under isothermal conditions at 25 °C using a Keithley 6487 picoammeter (both two-electrode and four-electrode schemes were used).

The dielectric spectra were obtained using a "Concept 22" broadband dielectric spectrometer (Novocontrol Technologies) equipped with an ALPHA-ANB high-resolution automatic frequency analyser. Dielectric permittivity and dielectric loss were measured in the frequency range of $1–10^6$ Hz; the input signal amplitude was 1 V. Before measurements, platinum electrodes 10 nm thick were placed onto the samples.

Results and discussion

The structure of the initial chitosan and the composites was studied using a SEM. SEM images of the chitosan film and the SWCNT-containing composite films are shown in Fig. 2. The structure of a chito-

san film (Fig. 2) contains lamellar elements, matching the data given in (Dobrovolskaya et al. 2018; Dresvyanina et al. 2020). The film containing 0.5 wt.% of SWCNT (Fig. 2) has a denser and more homogeneous structure.

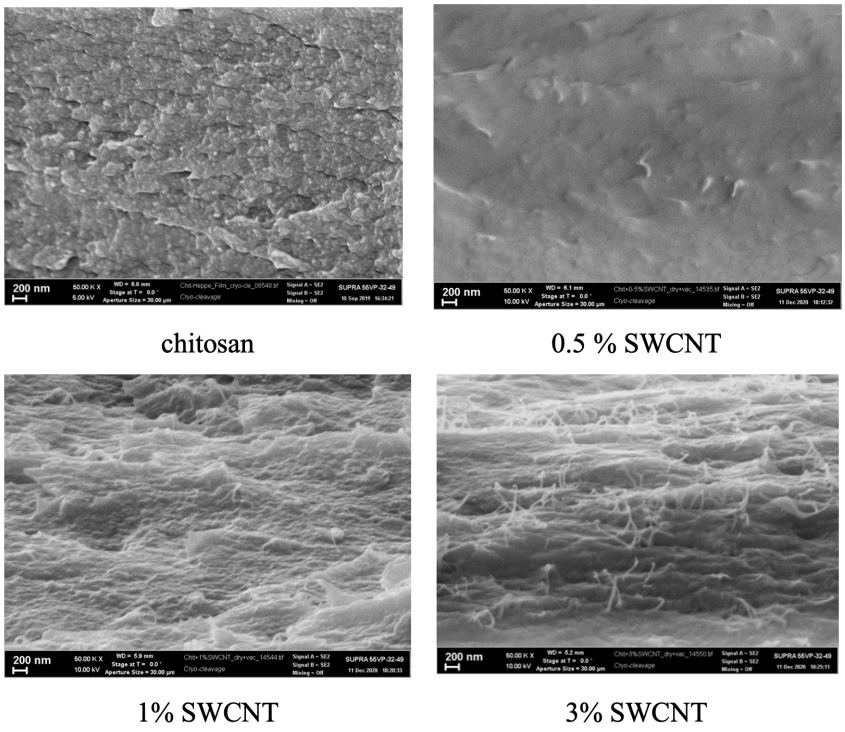

Fig. 2. SEM images of the chitosan film and the SWCNT-containing composite films

When the content of SWCNT in the composite reaches 1.0%, individual carbon nanotubes can be seen on the fracture surface (Fig. 2). The amount of nanotubes on fracture surface increases in the sample with 3% SWCNT (Fig. 2). This conducting filler structure should result in high conductivity of the composite material.

Fig. 3 shows that the increase in SWCNT content from 0.5 wt.% to 1.0 wt.% leads to an increase in the conductivity of the composite film (from 10^{-6} to 10^{-2} S/m). A sharp increase in the conductivity of the material with a slight change in the content of the filler indicates the formation of the conductivity percolation threshold.

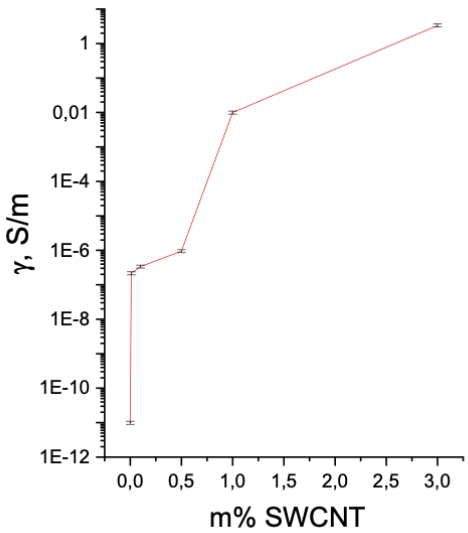

Fig. 3. The volume conductivity of chitosan-based composite films versus SWCNT mass percentage

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The further increase in filler mass concentration (up to 3 m%) leads to a significantly slower increase in sample conductivity due to the formation of a grid-like SWCNT structure in the bulk of chitosan.

Fig. 4 shows frequency dependences of $\varepsilon''(f)$ of the composite samples.

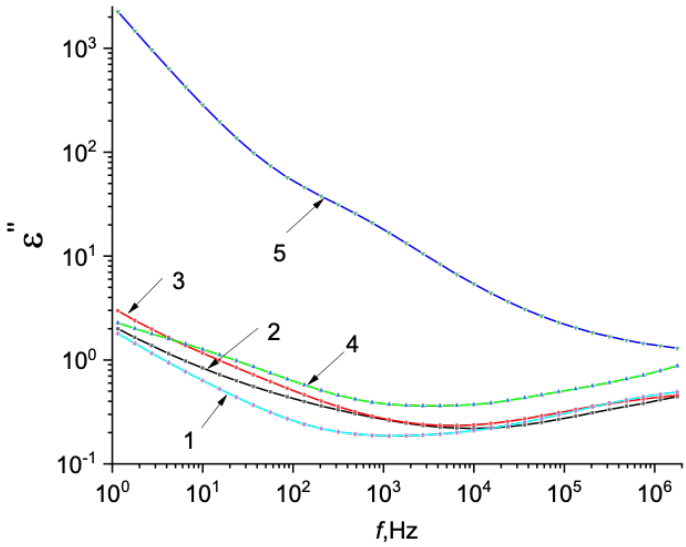

Fig. 4. Frequency dependences of the $\varepsilon''(f)$ of the composite samples (SWCNT m% 0 (1), 0.01 (2), 0.1 (3), 0.5 (4) and 1.0 (5))

The plot suggests that the initial chitosan films have the lowest dielectric loss value (0.03 at 1 kHz). With the increase in the SWCNT concentration, dielectric loss increases to 0.68. The dielectric loss of the sample with 1% SWCNT is much higher due to the increase in the sample's conductivity. The maximum value of dielectric loss is probably tied to Maxwell—Wagner—Sillars (MWS) polarisation (Maxwell 1873). The surface boundary between SWCNT and chitosan can be described as multiple nanocapacitors, their stored charge is determined by the difference between the conductivities of SWCNT and chitosan (Xia et al. 2017).

Fig. 5 shows that with an increase in SWCNT concentration from 0 m% to 5 m%, composite relative dielectric permittivity increases from 4.4 to 5.7 at 1 MHz. The results achieved are in line with the study (Bonardd, Robles, Barandiaran et al. 2018), where ε' ranges from 6.5 to 5.5 in the frequency range from 1 kHz to 1 MHz.

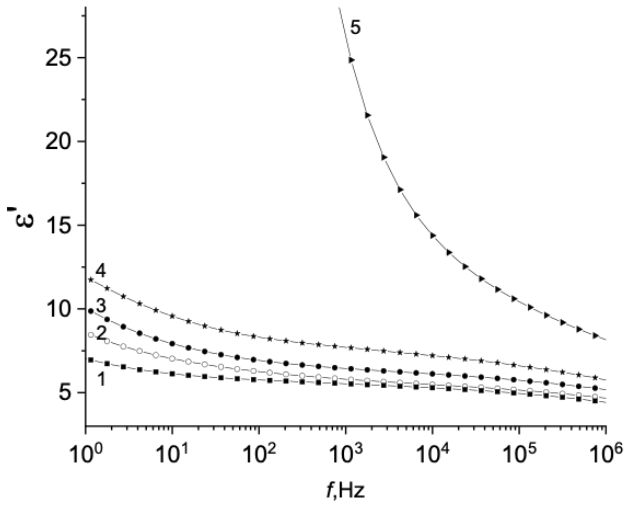

Fig. 5. Frequency dependences of the relative dielectric permittivity of composite samples (SWCNT m% 0 (1), 0.01 (2), 0.1 (3), 0.5 (4) and 1.0 (5))

The inscrease in SWCNT mass concentration up to 1 %m leads to a notable increase in relative dielectric permittivity in the low-frequency range; with the increase of the frequency the relative permittivity decreases.

It is a known fact that chitosan films have high hygroscopic properties, which can affect their relative dielectric permittivity. Fig. 6 shows the dependences between relative permittivity and filler mass percentage. These dependences were achieved at 80 °C, but the drying times were different for curves 2–3.

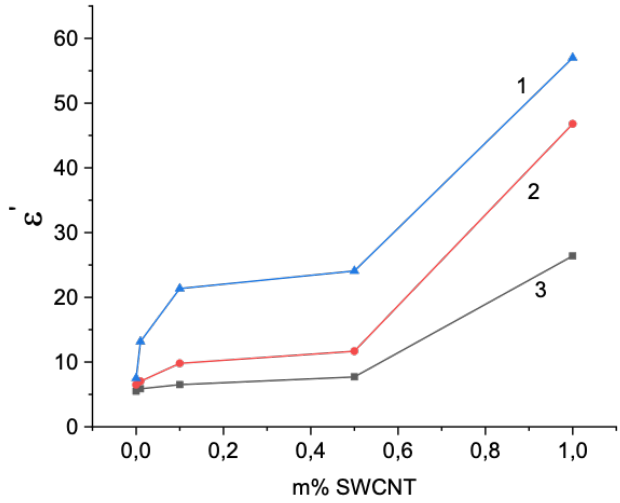

Fig. 6. The relative permittivity versus filler mass percentage at 1 kHz (Drying times: 0 hours (1), 1.5 hours (2) and 3 hours (3))

The plot suggests that the relative permittivity of dried films is lower, this difference is due to water sorption in films that have not been dried.

Conclusion

Biocompatible composite chitosan films with single-walled carbon nanotubes have been obtained. The dependences between their electrophysical properties and nanotube concentrations have been established.

SWCNT insertion promotes chitosan structure ordering and the formation of a denser macromolecule packing. It is shown that with an increase in SWCNT content from 0 to 3 wt.%, electrical conductivity changes from 10^{-11} to 10 S/m. The conductivity percolation threshold is in the range of 0.5–1 wt.%.

It is established that a sharp increase in dielectric losses is observed with an increase in SWCNT concentration above 0.5% by weight. The increase in dielectric losses and permitivity in the low frequency region is due to MVS polarisation. The results obtained make it possible to expand the potential applications of this biocompatible electrically conductive material in tissue engineering.

Conflict of interest

The authors declare that there is no conflict of interest, either existing or potential.

Author contributions

Almaz M. Kamalov and Margarita E. Borisova were involved in conceptualising and conducting the study, writing the original draft and project management. Vera V. Kodolova-Chukhontseva, Elena M. Ivan'kova and Vladimir V. Yudin were involved in conducting the study and reviewing and editing the article.

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