Investigation of the spectral properties of media based on chitosan and carbon nanotubes

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Introduction

Common diseases of the cardiovascular system include pathological changes in connective tissue structures of the heart and large blood vessels due to atherosclerosis, inflammatory lesions, congenital inferiority or mechanical damage. These diseases led to the development of methods for creating tissue-engineered structures implanted in the area of damage to the tissues of the heart and blood vessels [1]. Such methods involve the formation of a three-dimensional biocompatible scaffold with its subsequent filling with living cells. One of the most effective and modern methods of creating such scaffolds is laser printing.

Biological and synthetic materials are used to create cellular and tissue engineering structures for the restoration of the cardiovascular system [2]. However, biological materials have deficiencies associated with the possibility of transmission of infections, and synthetic compounds do not provide the necessary mechanical and bioresorbtion characteristics. In view of this, there is a need for new materials for tissue engineering in the field of the cardiovascular system.

To create the considered structures it is proposed to use chitosan, basically this aminosugar is used as a matrix medium for fillers in the form of functional particles [3, 4]. The addition of carbon nanotubes to natural or synthetic polymer structures enhances the mechanical properties and enhances the electroconductive and physiological properties of the structure for restoring the tissues of the cardiovascular system [5].

In this paper, we present a study of chitosan-based samples with inclusions in the form of carbon nanotubes in order to use the composition as a starting material for the preparation of cellular and tissue-engineered structures used in cardiovascular surgery.

Materials and Methods

Two types of water-soluble chitosan, edible and succinate, were used in this study. Edible chitosan (EC) was obtained from high-molecular chitosan by chemical hydrolysis and was a cream colored powder with a main substance content of 88.4%, a moisture content of 3.13% and mineral substances of 0.53%. Chitosan succinate (CS) is derived from crab chitosan by interaction with succinic anhydride. The material was a pearl-cream powder with a residual moisture content of 4.79%, the pH of the aqueous solution was 7.7.

As a filler for the creation of samples, 2.7% aqueous paste based on single-walled carbon nanotubes (SWCNTs) was used. SWCNTs were obtained by gas-phase synthesis with a wash to 99% purity. The diameter of the tubes was 1-2 nm, the length exceeded 5 μm. The feature of nanoparticles was a high specific surface area – 420 m^2 / g.

Water dispersion media (dispersions) based on SWCNTs with EC and CS were obtained. First, SWCNTs were mixed on a magnetic stirrer for 20 minutes with distilled water to obtain a concentration of 10^{-5} %. The resulting dispersions were then subjected to a powerful ultrasonic field with a power amplitude of ~ 40 W for 50 min. Then a powder of EC and CS with a concentration of 1:49 was gradually added to the homogeneous dispersion of SWCNT. The mixture was then stirred in an ultrasonic bath with an operating frequency of 45 kHz for 40 minutes.

From the final dispersions obtained, film samples were prepared for the study by water evaporation upon the influence of laser radiation. A pulsed ytterbium laser (wavelength 1064 nm) and a semiconductor laser (970 nm wavelength) with a power of no more than 5 W were used as sources of laser radiation.

Raman spectra in the range 100-1800 cm-1 were measured using the LabRAM HR Evolution (Horiba) spectrometric complex. As a source of exciting radiation, a HeNe laser with a wavelength of 633 nm was used.

Absorption spectra of samples in the IR range 4000-400 cm-1 (2.5-25 μm) were obtained by the method of attenuation total reflection using the Nicolet iS50 Fourier spectrometer (Thermo).

Results

To study the degree of binding of the aqueous dispersion components of chitosan to carbon nanotubes (CNTs), characteristic amide bands on IR and Raman spectra of film samples were analyzed. To compare the spectra, control samples from pure components are prepared separately.

IR Spectra

Peaks on the spectrum of pure chitosan turned out to be shifted relative to the peaks of films based on chitosan and SWCNT, and their intensity was sharply changed, which indicates the molecules connection of substances among themselves. From the spectrum of EC (see fig. 1), it is seen that the intense peak near 3350 cm^{-1} is due to stretching vibrations O–H and H–H (stretching of bonds);

the band of about 2868 cm^{-1} is connected with the valence vibrations of the C–H bonds.

A group of bands from 500 cm^{-1} to 1660 cm^{-1} is characteristic of the amide group (Amide I-Amide VI bands). Amide I (about 1550 cm^{-1}) characterizes the vibrational ability of the amide group, in which a periodic elongation of the C=O bond occurs, which can be used to judge the degree of acetylation. Comparing with the analogous peak in fig. 2b, we can conclude that the CS degree of acetylation is higher.

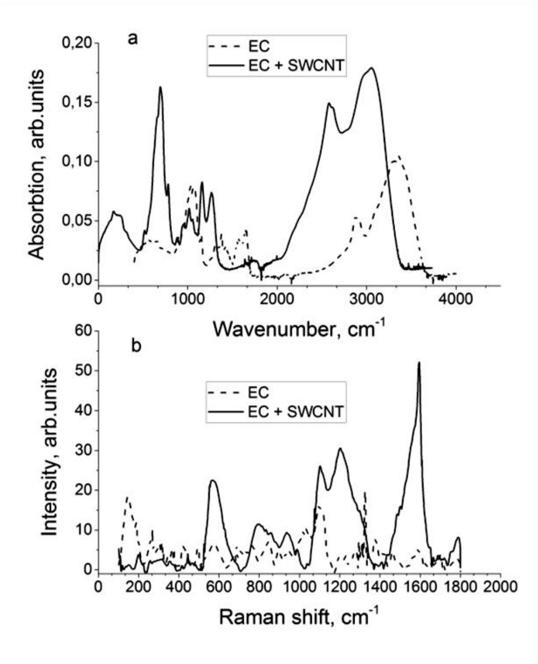

Figure 1: IR (a) and Raman (b) spectra of pure edible chitosan and with addition of CNTs

The absorption band of about 3450 cm^{-1} can be sensitive to adsorbed water, and an increase in the water content leads to an increase in the absorption band of about 1640 cm^{-1}, which was observed on the spectrum of EC with SWCNT. The difference in the intensity of the peaks near 3350 cm^{-1} and 1550 cm^{-1} in the CS spectrum is related to the degree of acetylation. Also, it is possible that the contribution of SWCNTs was more pronounced on the spectrum when connected to the EC.

A wider CS band of about 3350 cm^{-1} in comparison with EC could be associated with the stretching of the O–H bond, which overlaps the N–H stretching in the same region. It should be noted that intense peaks for CS with SWCNTs of about 1040 cm^{-1} and 1200 cm^{-1} are related to the stretching vibrations of C–C and C–O, which confirms the binding of the dispersion components to each other. A similar increase in intensity is observed for EC with SWCNT in the same region with respect to the spectrum of pure chitosan, however, the peak amplitudes are harsher than in the spectrum of CS. It is assumed that the penetration of SWCNTs into a more viscous gel-like structure of EC with a concentration of 2% was weaker than in the more liquid CS sample.

Raman Spectra

As seen in fig. 1b and 2b, the spectrum of chitosan with SWCNT is shifted relative to the initial chitosan spectrum, which indicates changes in the structure of amino sugars and tubes. These shifts are responsible for connecting the components of the dispersion to each other.

The bands of about 1603 cm^{-1} correspond to the deformation symmetric vibrations of the amino group. The shape of the peaks in the spectrum of EC with SWCNT is similar to that of the spectrum of CS with SWCNT, which is mainly due to a stronger manifestation of the contribution of nanotubes to the Raman spectrum in comparison with the spectra of organic substances.

Peaks with frequencies of about 1200 $cm^{-}1$ and 1120 cm^{-1} are responsible for the stretching vibrations of C–O and C–N, which were manifested in the spectra of EC and CS. These peaks shifted from their original position when chitosan was combined with the tubes, and their intensity increased sharply, which can be explained by the SWNT D mode that is strongly manifested in this region.

It should also be noted that SWCNTs exhibit semiconductor properties and do not have any structural damage, as can be seen from fig. 3b: the ratio of the intensity of the RBM mode (about 500 cm^{-1}), D and 2D modes (about 1200 cm^{-1} and 2800 cm^{-1}) with the G mode intensity (about 1594 cm^{-1}).

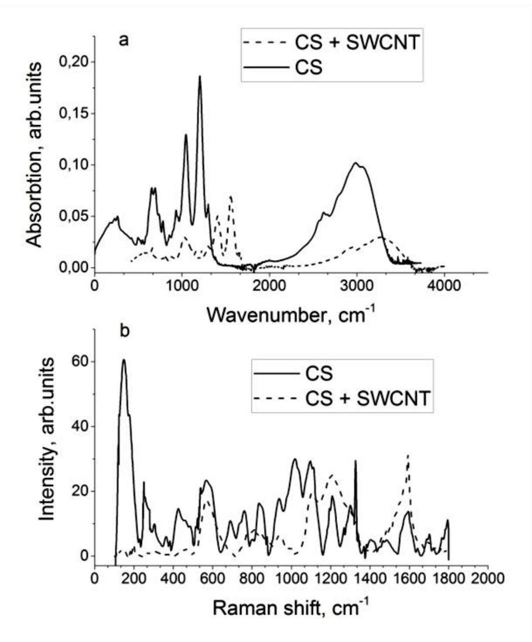

Figure 2: IR (a) and Raman (b) spectra of pure chitosan succinate and with addition of CNTs

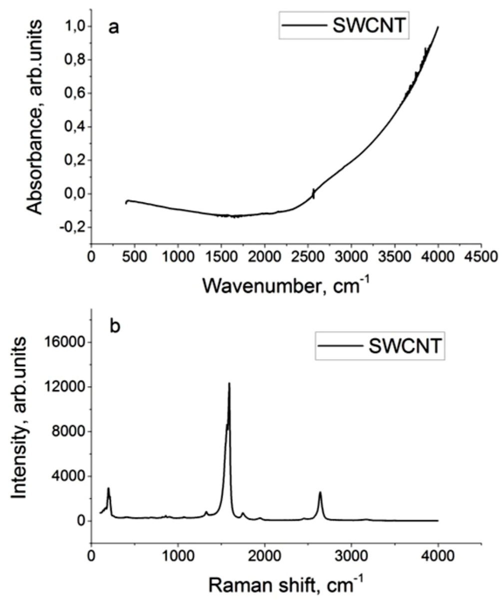

Figure 3: IR (a) and Raman (b) spectra of SWNTs

Discussion

For the study water dispersions of chitosan and dispersion of chitosan with carbon nanotubes were made. To investigate the properties of materials obtained from these dispersions, film samples were obtained by evaporating the aqueous component under the influence of laser radiation. Based on the results of the study using IR spectroscopy and Raman spectroscopy, it was found that changes in the structure of a sample based on chitosan and SWCNT occurred due to the appearance of intermolecular bonds. It was found that a higher degree of acetylation of CS leads to its more homogeneous dissolution, while EC is prone to gelling. The addition of carbon nanotubes is due to an increase in the hardness of the resulting samples.

Conclusions

Thus, the conducted researches are useful for manufacturing of three-dimensional cellular and tissue engineering designs used for restoration of defects of cardiovascular system.

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