PREPARATION AND PHYSICOCHEMICAL CHARACTERISTICS OF AN IODINE AND BISMUTH CONTAINING COMPOSITE MATERIAL BASED ON CHITOSAN

Anatoly Sklyar[1], Oksana Kalinkevich[1,a], Aleksei Kalinkevich[1,b,*], Vadym Chivanov[1,c]

[1] – Institute of Applied Physics, NAS of Ukraine, 58 Petropavlovska Str., 40000 Sumy, Ukraine
[a] – ORCID: 0000–0002–9631–2951, [b] – ORCID: 0000–0002–4793–7568,
[c] – ORCID: 0000–0001–5845–2315
[*]corresponding author: kalinkevich@gmail.com

Abstract

We created composite materials by using a straightforward method, combining chitosan, iodine, and bismuth. We used two chitosan with two different molecular masses. We used iodine in the composites as chitosan iodide and bismuth in the form of tetraiodobismuthanuide. We analysed the resulting materials with scanning electron microscopy, X-ray diffraction, temperature-programmed desorption mass spectrometry, and visible light spectroscopy. We observed that bismuth and iodine were evenly distributed throughout the composites and did not separate into distinct phases. These composite materials have the ability to form organised porous sponges, making them suitable for a wide range of applications in different fields.

Keywords: *bismuth, iodine, chitosan*

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1. Introduction

The structure of chitosan offers wide possibilities for its chemical transformation and modification to obtain materials with various structures and properties. The ability to biodegrade is of great interest and expands the prospects of using the obtained products in various fields. Research on chitosan and its derivatives for use in medicine and pharmacology is developing at a particularly fast pace. Chitin and chitosan exhibit great potential for medical uses due to their ability to inhibit bacterial growth, their compatibility with human tissues, and their capacity to promote wound healing processes. Numerous studies have highlighted these properties and their potential applications in medicine. Additionally, chitosan serves as a versatile foundation for developing a wide range of composite materials.

Iodine has a long history of medicinal use and is known for its powerful antibacterial properties. It effectively inhibits the growth of various types of microorganisms, including antibiotic-resistant bacteria, fungi, and certain viruses. When combined with organic substances, iodine has been found to exhibit antiviral effects. Combining chitosan and iodine in materials shows promise in overcoming microbial resistance to antimicrobial treatments by targeting multiple mechanisms of microbial cell stability. Although iodine's volatile nature can limit its use, this limitation can be overcome by attaching iodine to functionalised polymers. The utilisation of chitosan-iodine complexes has gained quite a bit of attention in various fields, both in terms of practical applications and structural and property investigations.

Bismuth induces the synthesis of low-molecular-weight proteins, participates in the ossification processes, and forms intracellular inclusions in the epithelium of renal tubules. Bismuth preparations are produced in the form of powders, ointments, pastes, pills, and suspensions. Bismuth preparations were used as means of therapy for the gastrointestinal tract already in the 16th century. Various preparations of bismuth (bismuth subcitrate, bismuth subsalicylate, bismuth subgallate, etc.) have been and continue to be used in clinical practice, but the most common is colloidal bismuth subcitrate [1]. Researchers have obtained bismuth complexes with other polymers (alginate and hyaluronic acid) as well as with carboxymethylchitosan and acid-soluble chitosan [2–8]. In addition, bismuth in combination with chitosan is used to create biosensors. Nanoparticles of bismuth oxide (Bi_2O_3) and chitosan have been used to create a sensor to determine DNA hybridisation [9], electrodes with bismuth-chitosan coating have been used to determine the concentration of food azo dyes [10], and carboxymethylchitosan with bismuth has been proposed to create electrodes to determine heavy metal concentrations [11]. Obtaining new bismuth preparations is especially important due to the development of *Helicobacter pylori* resistance to metronidazole and clarithromycin [12].

We aimed to obtain composite materials based on chitosan containing iodine and bismuth in the form of solutions as well as solid porous sponges.

2. Materials and Methods

Chitosan with a degree of deacetylation of 82% and a molecular mass of 300 kDa was purchased from YuDa (China) and was used without further purification. Bismuth/chitosan material was obtained by using chitosan iodide. The salt of chitosan and hydroiodic acid was obtained according to a previously developed method [13]. In parallel, a solution of bismuth(III) dihydroxide nitrate was prepared. The dissolution of the salt occurs with the formation of an intermediate water-insoluble bismuth(III) iodide, black in colour, that is formed in the first stage. This precipitate dissolves further in an excess of iodide acid,

which is added until the complete dissolution of the precipitate, with the formation of the $H[BiI_4]$ complex:

$$Bi(OH)_2NO_3 + 3HI \rightarrow BiI_3\downarrow + HNO_3 + 2H_2O \quad (1)$$

$$BiI_3 + HI(s) \rightarrow H[BiI_4]. \quad (2)$$

The resulting solution of the bismuth complex salt solution was added dropwise to the chitosan solution in hydroiodic acid at 55°C with active stirring.

Chitosan of different molecular masses (200 and 500 kDa) was used to obtain the material. The chitosan concentration in the resulting solution was 3% (w/w); the molarity of $H[BiI_4]$ was 0.0014 M.

The solutions were freeze-dried to obtain the porous material in the form of a sponge.

Scanning electron microscopy (SEO-SEM Inspect S50-B, SEO, Ukraine) and X-ray diffraction (DRON-4, Burevestnik, Russia) were used to study the physicochemical properties. Temperature-programmed desorption mass spectrometry (TPDMS) analysis was carried out at a specialised installation of the Institute of Applied Physics of the National Academy of Sciences of Ukraine. Absorption spectra in the visible part of the spectrum were recorded on a SPEKOL-1500 spectrophotometer (Germany).

3. Results and Discussion

Freeze-dried sponges are very fragile and easily crumble into powder. Electron micrographs show particles of powder and fragments of sponge plates (Figure 1).

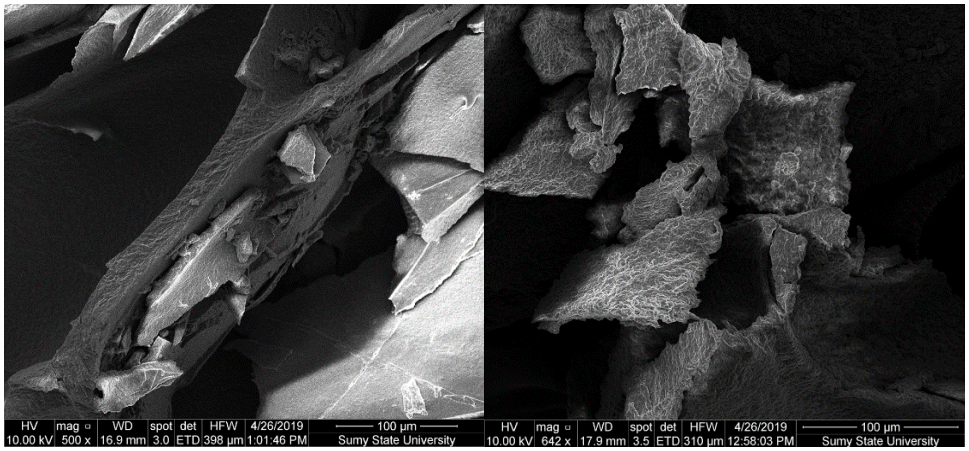

Figure 1. Scanning electron micrographs of chitosan-bismuth-iodine sponges. The sponges were made of chitosan with a molecular mass of 200 (left) and 500 kDa (right).

X-ray diffraction of the samples at a 2θ angles of 10°–90° indicated that neither sample contains crystalline phases (there are no diffraction peaks; diffractograms not shown). Therefore, the introduced compound is bound to the polymer and does not crystallise into a separate fraction. The obtained material is amorphous.

Figures 2 and 3 show the thermograms (temperature profiles) of the yield of ions with m/z 18 ($[H_2O]^+$) and 143 ($[IO]^+$). Bismuth (atomic mass 209) is beyond the mass range of the mass spectrometer used for this study. More iodine was released from the iodine- and

bismuth-containing samples with 500 kDa chitosan, and there was also a high-temperature tail for ions with m/z 143 ($[IO]^+$). The maximum output of iodine and water occurred at 200°C. This position of the maximum iodine yield indicates that the iodine in the samples is in the bound state (if free iodine is present in a sample, it is released at much lower temperatures, namely 50–100°C).

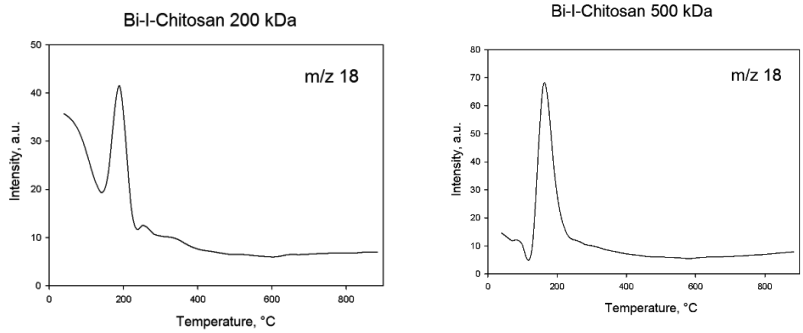

Figure 2. The thermal profile of the m/z 18 ion release from chitosan-bismuth-iodine sponges. The sponges were made of chitosan with a molecular mass of 200 or 500 kDa.

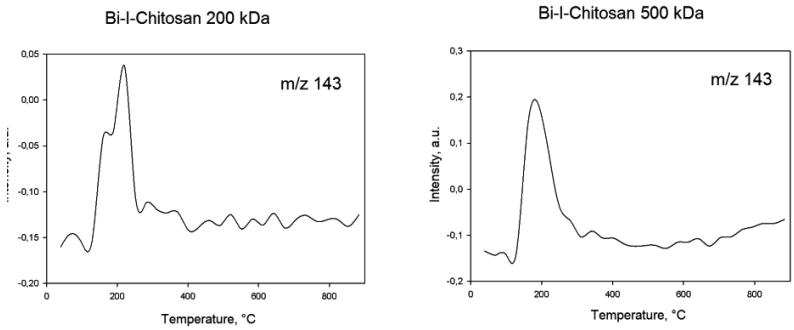

Figure 3. The thermal profile of the m/z 143 ion release from chitosan-bismuth-iodine sponges. The sponges were made of chitosan with a molecular mass of 200 or 500 kDa.

The samples are hygroscopic – they readily absorb moisture from the air – and during storage, iodine vapours are released from them (most likely in the form of molecular iodine). However, the sponge made of 200 kDa chitosan show greater affinity for water. This may be due to the different reasons, as the chitosan of different molecular masses have the same degree of deacetylation but they are not standardised and could be have different origins. It should be noted that the samples of pure 200 and 500 kDa chitosan show the same hygroscopicity. The thermogram of a sample made with 200 kDa chitosan shows the release of unbound water at low temperatures (drying). The sample of the material made of 500 kDa chitosan shows only the release of the bound water at ~200°C, although we stored all samples in similar conditions.

Figure 4 shows the absorption spectra of the initial iodine- and bismuth-containing chitosan solutions (dotted line) and the spectra of the sponge-like materials obtained after dissolution of the materials in water (solid line).

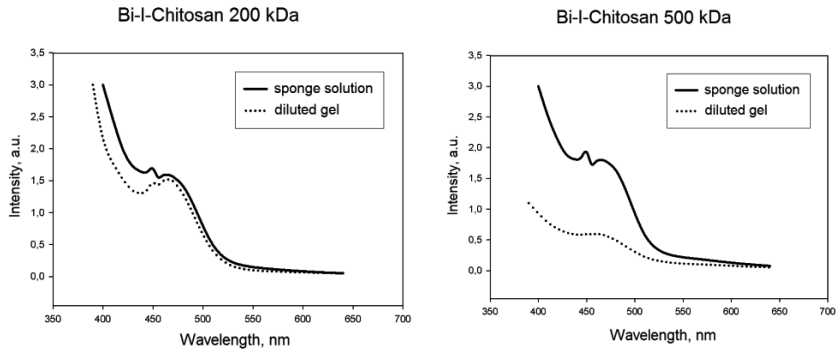

Figure 4. Visible light absorption spectra of iodine- and bismuth-containing materials based on chitosan with a molecular mass of 200 and 500 kDa.

The peaks at 465 nm correspond to the absorption spectrum of the complex tetraiodobismuthanuide anion $[BiI_4]^-$ [14]. So, the analysis indicates the presence of both $[BiI_4]^-$ (according to optical spectroscopy data) and I^- (according to the TPDMS data) in the obtained composite materials. Such a complex preparation can be used to create medical devices and preparations and to develop biosensors or smart materials like components of non-toxic light-harvesting layers in environmentally friendly photovoltaic and optoelectronic devices [15].

4. Conclusions

We synthesised two new composite materials based on chitosan iodide comprising bismuth in the form of the complex tetraiodobismuthanuide anion $[BiI_4]^-$ and iodine using chitosan with two molecular masses (200 and 500 kDa) as a polymer base. The porous sponges made from these materials are very fragile and hygroscopic. These materials could be used in various fields, including biomedical applications and smart materials for environmentally friendly electronics.

5. Acknowledgements

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