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THE SYNTHESIS OF NEW POLYMER COMPOSITES BASED ON OIL PORPHYRINS

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Abstract: *This research on the synthesis of composite materials based on heavy oil residues possesses scientific novelty in several aspects. In the contemporary stage of industrial development, the increasing waste load of the oil refining industry, along with the growing demand for high-performance and durable materials, necessitates new approaches for scientific and technological advancement. For the first time, polymer composites have been developed based on petroleum porphyrins isolated from asphaltene–resin–paraffin residues. A new synthesis method for polymer composite materials based on petroleum porphyrins isolated from the asphaltene–resin–paraffin residues of the Buzovna field has been proposed. This approach contributes to solving the environmental problem associated with the utilization of heavy oil residues. The observed spectroscopic changes can be explained by the fact that the immobilization of the porphyrin occurs through the formation of ionic bonds between the functional groups of the porphyrin and the positively charged nitrogen atoms of chitosan, resulting in the formation of an insoluble polyelectrolyte complex. Thus, the results indicate that only chitosan effectively binds to the porphyrin, whereas methylcellulose remains inert.*
Keywords: *composite material, oil residues, chitosan, methylcellulose, biocompatible polymer.*

INTRODUCTION

The effectiveness of drugs can be enhanced through their immobilization in polymer carriers. The use of polymers enables the imparting of important properties to already known drugs, such as increased stability, controlled solubility, and reduced toxicity. In the future, applied studies on the physiological activity of polymers should lead to the development and introduction into practical medicine of a new generation of pharmaceuticals characterized by prolonged action, controlled pharmacokinetics, and targeted delivery to specific organs.

An important application area of porphyrins and their analogues is medicine. Based on their preferential accumulation in tumor cells and their photoluminescent ability to generate cytotoxic oxygen, research on porphyrins as sensitizers for the photodynamic therapy of oncological diseases is developing intensively.

However, despite their many positive qualities, porphyrins exhibit only short-term therapeutic effects, which necessitates frequent administration. To achieve prolonged drug action, viscosity regulators are employed, and the use of a new polymer form in the shape of a film, based on biologically active substances containing pharmaceuticals derived from petrochemical synthesis, has been proposed.

In ophthalmology, the most commonly used dosage forms are eye drops (solutions, suspensions), ointments and gels, as well as ocular films. The search for new drug forms that allow reduced administration without diminishing therapeutic efficacy

is of great scientific and practical interest. The use of long-acting drug formulations decreases the likelihood of overdose and mitigates the adverse effects of frequent instillations, while also relieving patients and medical staff from repeated manipulations. In this regard, the development and application of ocular drug films would represent a rational solution to the problem of achieving prolonged therapeutic effects and ensuring the targeted delivery of effective antibiotics to ocular tissues.

The use of drugs in the form of ocular films reduces both ocular toxicity and systemic side effects, since the drug is gradually released from the films and delivered to the conjunctiva and cornea in a prolonged and uniform manner, while minimizing the amount lost through lacrimal drainage into the nasal cavity. The valuable properties of ocular drug films also include their stability, allowing storage for up to two years, high sterility, reduced risk of infection, ease of placement on the conjunctival membrane, and lower drug consumption due to less frequent administration compared to eye drops. Furthermore, immobilization of drugs within films eliminates disadvantages such as the unpleasant taste of bitter or nauseating medicines, ensures their targeted delivery to the desired area of the body, and provides the basis for the development of various diagnostic products. A wide range of synthetic and natural polymers is widely used as materials for the production of such films.

Porphyrins are included in the composition of many drugs; however, as is well known, all drugs have a limited duration of action after which they are eliminated from the body. Moreover, the smaller the molecular weight of the drug, the faster it is excreted. For prolonged pharmacological effects, it has been proposed to graft physiologically active compounds with hydrolyzable ester bonds, salts, and other functional groups onto carrier polymers.

One of the rapidly developing areas in recent years is the fixation of active metalloporphyrins into polymer matrices. A review of the literature shows that the mode of attachment of porphyrins to polymer matrices is diverse. In several studies, the immobilization of porphyrins and their complexes was achieved through coordination bonds. The interaction of porphyrins with polymers occurs via the formation of secondary amines, esters, and other functional groups as a result of the interaction between the functional groups of polymers and porphyrins. In these works, the immobilization of porphyrins and metal complexes was confirmed using electronic and IR spectroscopy, elemental analysis for nitrogen, as well as spectrophotometric methods to determine the mass fractions of metals in polymer metalloporphyrins.

The analysis of the literature indicates that polymer-bound porphyrins are significant in terms of their therapeutic effects. Nevertheless, research on the synthesis of porphyrins and their metal derivatives remains limited. Therefore, the development of new methods for immobilizing porphyrins and their metal derivatives in polymer matrices, along with expanding their application fields, is undoubtedly of great interest.

Furthermore, the potential modification of metalloporphyrins derived from heavy petroleum residues may stimulate the advancement of more efficient and cost-effective technologies for the production of effective pharmaceuticals.

EXPERIMENTAL PART

The research object was the ASPO collected from the Buzovna field of “Tagiyev Operating Company” Intertek Azeri LTD. The content of asphaltenes, resins, and

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paraffins in the field samples was determined according to GOST 11851-85 “Oil. Method for the determination of paraffin.”

X-ray fluorescence analysis of solid deposits was carried out using an X-ray fluorescence spectrometer to determine the presence and quantitative composition of metals in ASPO. Sample measurements were conducted in the range of 0.0–16.0 keV.

IR spectroscopy analysis was performed at 20 °C using a NICOLET 5700 FT-IR Fourier transform infrared spectrometer in the range of 400–4000 cm^{-1}. Paraffin, asphaltene, resin, and composite samples were pressed into KBr pellets. The baseline correction was conducted using the OPUS software.

UV spectrometry analysis of free porphyrins, collected in 10 ml fractions at the outlet of the cylinder, was performed on an Evolution 300 UV/VIS spectrophotometer (USA) using quartz cuvettes with a thickness of 10 mm at 700 nm. The spectral type of porphyrins was determined by the ratio of the intensities of the I, II, III, and IV absorption bands.

The UV spectra of aqueous solutions of drugs were also recorded on an Evolution 300 UV/VIS spectrophotometer (USA) using 10 mm quartz cuvettes. The drug concentrations were determined using calibration curves based on the absorption maxima characteristic of each drug.

For the preparation of a chitosan/methylcellulose composite material based on petroleum porphyrins, chitosan and methylcellulose were used as raw materials, and the process was carried out using the methods described below.

Chitosan (Chitosan, Practical Grade from Crab Shells) with a molecular mass of 3.5–250 kDa and a degree of deacetylation of 70 (fig.1.) was produced by Sigma (USA) and used without additional purification.

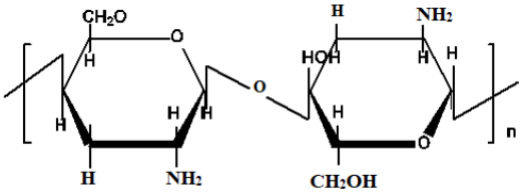

Fig. 1. The chemical structure of chitosan

Methylcellulose (MC) (fig.2.) was produced by Sigma (USA) and used without additional purification.

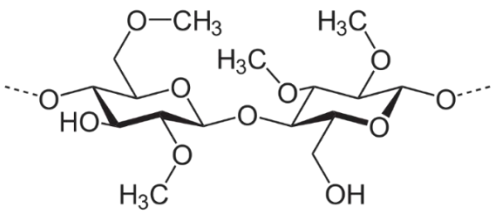

Fig. 2. Chemical structure of methylcellulose

Polyvinyl alcohol (PVA) with a molecular weight of 90 kDa, produced by Sigma (USA), was used without additional purification. It has a degree of hydrolysis of 86.7–

88.7 mol% and a residual acetate group content of 10.0–11.6%. PVA dissolves in water when heated up to 60 °C.

A 2% chitosan solution was prepared in 0.1 M acetic acid in a beaker, which was then placed on a magnetic stirrer until the chitosan was completely dissolved. Separately, a 1% methylcellulose solution was prepared by dissolving it in distilled water. The polymer ratio was set at 75:25. The calculated amount of porphyrin (150 mg/g) was added to the filtered polymer solution under stirring. The resulting polymer solution was poured into Petri dishes and dried at room temperature for 2–3 days. The dried biopolymer samples were carefully removed from the Petri dishes and placed in a 5% NaOH solution to neutralize residual acetic acid, followed by washing with ethanol to remove excess alkali. The modified samples were then rinsed with distilled water and dried in air.

Method for the preparation of polymer composites containing Mitomycin-C:

Upon heating, a 1.5% chitosan solution was prepared by dissolving chitosan in 0.1 M hydrochloric acid. The solution was placed on a magnetic stirrer until the chitosan was completely dissolved. Separately, an 8% PVA solution was prepared in distilled water. The cooled 1.5% chitosan solution was then combined with the PVA solution. The polymer ratio was set at 75:25. The calculated amount of immobilized Mitomycin-C (125 mg/g and 250 mg/g) was added to the filtered polymer solution under stirring. The resulting solution was poured into Petri dishes and left on a horizontal surface at room temperature for 2–3 days. The obtained dry composite samples were carefully removed from the molds, immersed in a 5% NaOH solution to neutralize residual acid, and subsequently washed with ethanol to remove excess NaOH.

To obtain cross-linked films, 2% chitosan was dissolved in an aqueous 1% hydrochloric acid solution upon heating and then stirred on a magnetic stirrer for 4–5 hours. The calculated amount of immobilized Mitomycin-C (125 mg/g) was added to the filtered polymer solution under stirring. For subsequent cross-linking, an aqueous 0.05% glutaraldehyde solution was added to the polymer solution containing Mitomycin-C. The resulting polymer solution was poured into Petri dishes and dried at room temperature for 2–3 days. The dried biopolymer composites were carefully removed from the Petri dishes, immersed in a 5% NaOH solution to neutralize residual acetic acid, and then washed with ethanol to remove excess alkali.

A 1.5% chitosan solution was combined with an 8% polyvinyl alcohol solution. The polymer ratio was set at 75:25. The anticancer drug Mitomycin-C (125 mg/g and 250 mg/g) was then added to the resulting polymer solution.

RESULTS AND DISCUSSION

One of the approaches to enhancing the effectiveness of cancer chemotherapy, particularly in the treatment of malignant neoplasms, is the use of new polymer composite systems in the form of films containing immobilized anticancer drugs. The implantation of such systems at the tumor site allows for the sustained generation of high concentrations of the drug directly in the vicinity of cancer cells.

The current arsenal of oncological agents is limited, and many of these drugs have several drawbacks, including a short duration of antitumor effect and systemic toxicity. One approach to overcoming these limitations is the use of fundamentally new polymer composite systems in the form of films based on petroleum porphyrins. These systems

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are employed in the treatment of cancers of various organs, including the lungs, eyes, ovaries, mammary glands, stomach, pancreas, and bladder, with their antitumor effects exerted directly on malignant tumor cells. Porphyrins are widely used as photosensitizers in the photodynamic therapy of cancer. These drugs are highly active but are characterized by a short duration of action (3–4 hours) and rapid elimination from the body. Among polysaccharides capable of forming films, chitosan is one of the most widely used in the pharmaceutical industry.

Chitosan (poly(1-4)-2-amino-2-deoxy-β-D-glucan)) is a natural polymer obtained through the alkaline deacetylation of chitin—a linear aminopolysaccharide composed of N-acetyl-2-amino-2-deoxy-D-glucopyranose—and protein compounds derived from other natural sources.

The mechanical and physical properties of biodegradable chitosan films can potentially be enhanced by the addition of suitable polysaccharides such as methylcellulose. This water-soluble cellulose derivative is widely used in the pharmaceutical, cosmetic, and food industries as a binder, thickener, or film stabilizer. Methylcellulose films are less rigid but more flexible compared to chitosan films, whereas chitosan–methylcellulose composite films exhibit intermediate mechanical strength characteristics.

In this study, a comprehensive physicochemical investigation of polymer compositions based on petroleum porphyrins was conducted. To assess the potential chemical interactions among the functional groups of chitosan, methylcellulose, and porphyrin, the infrared spectra of the samples (fig.3 and fiq.4) were recorded and analyzed.

Bands characteristic of chitosan were observed at 896, 948, 1034, 1076, 1152, 1324, 1378, and 1420 cm^{-1}. In the 1500–1700 cm^{-1} region, some changes occurred due to the binding of porphyrins. Specifically, two chitosan bands at 1586 cm^{-1} (NH_2) and 1651 cm^{-1} (Amide I) shifted to 1592 cm^{-1} and 1647 cm^{-1}, respectively.

The observed spectroscopic changes can be explained by the fact that the immobilization of porphyrin occurs through the formation of ionic bonds between the functional groups of porphyrin and the positively charged nitrogen atoms of chitosan, resulting in the formation of an insoluble polyelectrolyte complex.

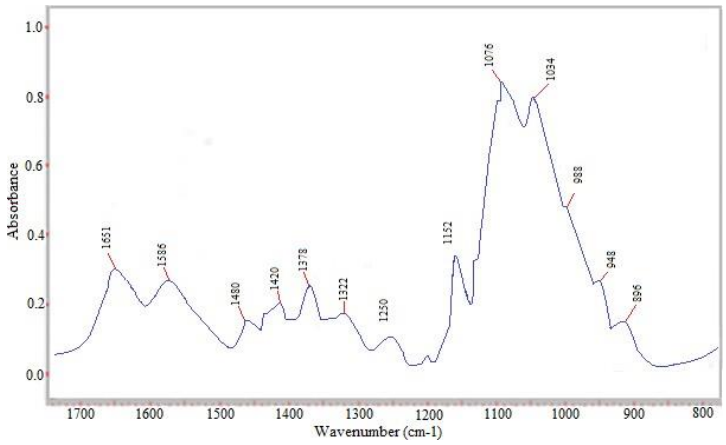

Fig. 3. IR spectra of the chitosan film

Thus, the results indicate that only chitosan binds effectively to porphyrin, whereas methylcellulose remains inert. The UV–visible (300–700 nm) absorption spectra of porphyrin and porphyrin-containing polymer films are shown in figure 5.

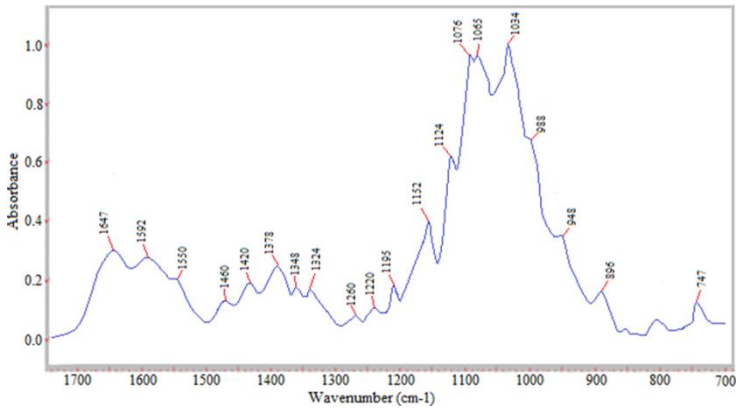

Fig. 4. IR spectra of porphyrin-containing biopolymer film

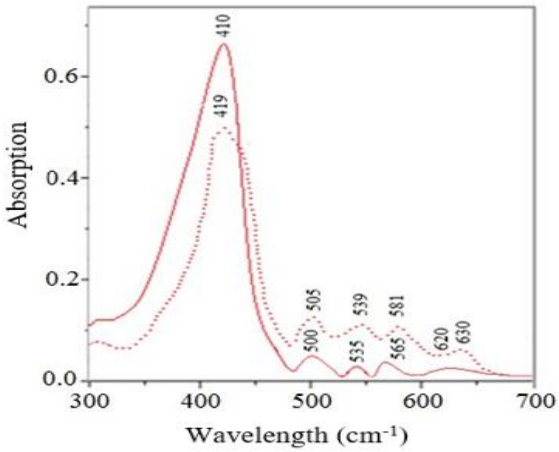

Fig.5. UV absorption spectra: porphyrin (solid), porphyrin-containing polysaccharide film

As seen from the figure, upon interaction with the polymer, the Soret band at 410 nm and the Q-bands of porphyrin (500, 535, 565, and 620 nm) are significantly shifted, indicating the formation of a complex. SEM images of the polymer composite systems are shown in figures 6 a and b.

SEM analysis confirmed that chitosan and chitosan–methylcellulose films possess smooth, uniform surfaces. This is attributed to the porphyrin molecules filling surface voids and smoothing the film surface.

The obtained data demonstrate the feasibility of using chitosan and methylcellulose polysaccharides to develop porphyrin-based film drug formulations. The characterized samples allow for the prediction of drug efficacy and the design of polymer materials that deliver the required amount of porphyrin to the body.

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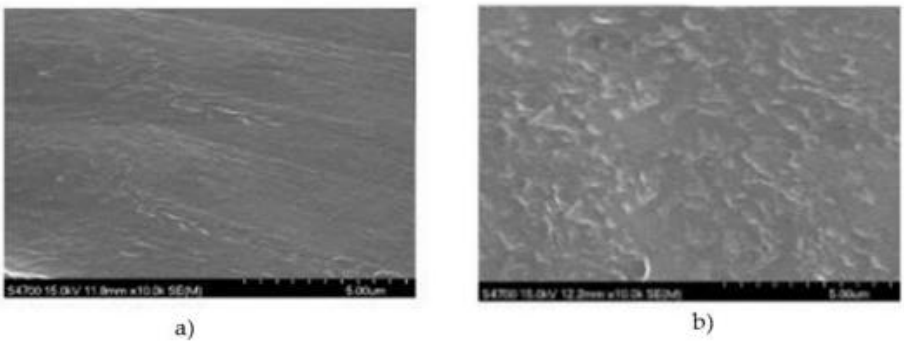

Fig. 6. SEM images of the polymer composites

a) Chitosan containing porphyrins; b) Porphyrin-containing chitosan/methylcellulose

Furthermore, the results of the physicochemical studies indicate that natural polysaccharide chitosan and the water-soluble polymer methylcellulose are highly effective as matrices for the development of new film materials for the treatment of oncological diseases.

CONCLUSION

A method has been developed for obtaining highly efficient extractants for the separation of metalloporphyrin concentrates from heavy petroleum products using highly selective bifunctional organic compounds (ketone alcohols) toward metal porphyrins. The best results were demonstrated by 2-hydroxycyclohexanone. Based on the results of spectral absorption in the visible region, it was established that in all obtained extracts the disappearance of characteristic absorption bands of vanadyl and nickel porphyrins and the appearance of bands characteristic of free porphyrin bases occurred, confirming the demetallization of metalloporphyrins during the extraction process.

The results of physicochemical studies demonstrated the high efficiency of using the natural polysaccharide chitosan and the water-soluble polymer methylcellulose as matrixs for the preparation of new composite materials.

The interaction mechanism of porphyrins with biocompatible polymers has been investigated in connection with the necessity of developing new effective anticancer and therapeutic drugs. Spectroscopic analysis revealed that porphyrin molecules exhibit strong affinity only toward chitosan, while methylcellulose remains inert, showing no interaction.

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