Influence of the nature of a polysaccharide on the surface-morphological and physico-mechanical properties of sol–gel plates

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Abstract. Thin-film sol–gel plates based on chitosan and glucomannan polysaccharides in a wide range of compositions were obtained. The effect of the polysaccharide component on the SEM surface morphology and physico-mechanical properties was evaluated. It was found that the introduction of the polysaccharide glucomannan (and/or Aloe Vera juice) into the composition of chitosan sol–gel plates increased the elastoplastic characteristics of the samples and had a significant effect on the surface relief of their solid phase. The obtained structures can be used for the design of bioadhesive sensor coatings with a high therapeutic effect, which is an urgent area for theranostics and regenerative medicine.

1. Introduction

The use of biopolymers, e.g. natural polysaccharides, makes it possible to form photonic materials in the form of thin-film coatings and plates for use as selectively sensitive biosensors in functional nanomaterials [1]. In addition, the polysaccharide matrix contributes to the provision of an active biointerface of bionanocomposites with body tissues.

Sol–gel synthesis is a technique for obtaining such materials of varying degrees of structuring (particles, layers, and 3D structures). It has a number of advantages over traditional methods and makes it possible to obtain optically transparent organic–inorganic composites with the possibility of incorporating functional additives of various natures into the matrix [3]. The use of silicon tetruglycerolate Si(OGly)₄, a pharmacologically active gel precursor, allows one-pot sol–gel synthesis of hybrid hydrogels under conditions close to physiological ones [4–5]. The use of biologically active polysaccharides such as cationic chitosan (CS) and neutral glucomannan (GM), as well as their mixtures as a matrix, contributes to the expansion of the application fields of the sol–gel materials obtained. These polymers are thermodynamically compatible, have the ability to gelation due to the formation of intermolecular contacts [6–8] and, importantly, are biocompatible and capable of biodegradation. In our recent study [9], the effect of the plant-derived therapeutic agent of Aloe Vera juice (AV, dry extract contains ~55% GM), a functional additive, on the surface morphology of sol–gel plates based on CS ascorbate, promising for the design of specific optical sensors and optodes of biomedical applications, was found. In this study, AV was used as the source of GM.

The microrelief and surface roughness parameters, as well as some physicochemical properties (surface energy, sorption capacity, adhesion, etc.) of hydrogel systems are known to largely determine the useful properties of the material [10]. In this connection, the control of the morphostructure of organic–inorganic hydrogels is topical when designing materials with desired properties for new
technological applications. SEM imaging is most commonly used for surface inspection due to its accessibility, relative ease of sample preparation and result interpretation.

This study examines the effect of the nature of the polysaccharide (cationic chitosan or neutral glucomannan) on the surface-morphological, sorption and physicochemical properties of the sol-gel plates.

2. Methodology

The following reagents were used: chitosan (CS) with a viscosity average molecular weight 32 kDa, a degree of deacetylation 80 mol.% (Golden Shell, CN); glucomannan (GM, Uspekh Corp, RU); poly(vinyl alcohol) with a weight average molecular weight of 80 kDa a degree of hydrolysis 85 mol.% (PVA, Titan Corp, RU); glycerol solution of Si(Ogly)$_4$ (IOS UB RAS, RU); ascorbic and aminocaproic acids (AscA and AmA, Khimreaktiv Corp, RU); 95% ethyl alcohol (RFK Corp, RU); Aloe Vera leaves and distilled water.

To prepare 15 wt% CS stock solutions in 3% AscA and 3% AmA, a sample of polymer powder was suspended in water on a magnetic stirrer, followed by addition of an air-dry AscA and AmA powders. The system was left at 20±2°C for 1 day in the absence of natural light until complete dissolution.

Aqueous GM solutions of a concentration of 0.5 wt% were prepared by suspending a sample of polymer powder in water on a magnetic stirrer at 80±5°C during 1 hour.

Aloe Vera juice (AV) was obtained in the laboratory by mechanical extraction of previously washed leaves of a 3-year-old plant, followed by filtration. The obtained AV was used directly immediately or stored until 7 days at 4±0.5°C in the absence of natural light.

Aqueous PVA solutions (biointert structure-forming component) of a concentration of 8 wt% were prepared by suspending a sample of polymer powder in the calculated amount of water on a magnetic stirrer for 5 min, followed by 850 W microwave treatment in a laboratory microwave system Mars-5 (CEM Corporation, US) during 60 s.

Sol–gel plates were prepared by mixing the polysaccaride component, the PVA solution and Si(Ogly)$_4$ in a 6 : 1 : 1 weight ratio (Figure 1). The composition of the polysaccharide component was varied by the ratio of the initial solutions CS and/or GM and/or AV in the mixture. The mixtures were thoroughly stirred for 4−5 min until homogeneity, placed on a horizontal silicone substrate at a rate of 0.5±0.1 mL/cm$^2$ and allowed for sol–gel process to proceed at 20±2°C. Gelation was carried out in a thin (4±1 mm) layer within 1−3 days. The solid phase (xerogels) was isolated by exhaustive extraction with ethyl alcohol within 7 days followed by drying at 20±5°C.

Figure 1. Scheme of the sol–gel plates preparation.

Sorption properties were assessed gravimetrically (Ohaus Adventurer AR 1530 scales, US) in H$_2$O vapor at 22±1°C. The sorption degree of water vapor ($S_w$, wt%) and the diffusion coefficients of the initial and final stages of sorption ($D_1$ and $D_2$, cm$^2$/s) were determined according to the standard method. The resorption rate was estimated by the immersion method based on the loss of structure integrity upon exposure to model media with pH = 1.1, 6.5, and 7.4 at 37±0.5°C.

Elastoplastic properties were evaluated on an Instron 3342 tensile testing machine (DE) used a 0.5 kN load cell in a uniaxial tensile mode at a speed of 10 mm/min. The breaking stress ($\sigma_b$, MPa),
Young’s modulus (E, MPa) and the elongation at break (εb, %) were calculated from the averaged data «stress–strain» curves (σ–ε) of 10 replicate measurements by standard procedures. Statistical data processing was performed using BLUEHILL-3 INSTRON software. Physicomechanical characteristics were calculated taking into account the initial length and thickness of the sample. The thickness of plates was measured with an Electronic Digital Outside Micrometer CT 200-521 (CN) with a 10 μm division and was expressed as the arithmetic mean of 10 measurements.

SEM images were taken on a MIRA\LMU scanning electron microscope (Tescan, CZ) at a voltage of 7 kV and a conducting current of 400 pA. A 5 nm thick gold layer was deposited on each sample using a K450X Carbon Coater (DE).

3. Results and discussion

It has been shown that as a result of gelation of the precursor Si(OGly)n, flexible monolithic hydrogel coatings are formed on the polysaccharide matrix (Figure 1). They possess a pH-dependent behavior characteristic of physically cross-linked hydrogels: the sorption capacity and the resorption rate of hydrogel plates at neutral pH are higher than in media with pH = 1.1 and 7.4. Complete resorption of samples in model biological media was observed after 3 days on average.

The assessment of the sorption properties of our sol–gel plates has shown that the water vapor diffusion in the polymer matrix does not obey Fick’s law and proceeds in an anomalous mode. The diffusion coefficients calculated from the initial (D1) and final regions (D2) of the kinetic curves of sorption differ by an order of magnitude (Table 1). For the plates based on a neutral polysaccharide (AV and/or GM), higher values of both diffusion coefficients and the sorption degree are observed in comparison with the compositions containing the amino polysaccharide CS. It is possible that the diffusion characteristics are affected by the change in the supramolecular structure of the samples due to variation in the polysaccharide component composition [11].

| Polysaccharide component CS : AV : GM | Water vapor sorption parameter D1 \(10^9\) D2 \(10^{10}\) \(S_w\) (wt%) | Physicomechanical parameter \(\sigma_b\) (MPa) | \(\varepsilon_b\) (%) | E (MPa) |
|--------------------------------------|---------------------------------|-----------------|---------------|--------|
| 0 : 0 : 6                           | 5.71                           | 13.5            | 77            | 0.12   | 6.54  | 0.011 |
| 3 : 0 : 3                           | 3.47                           | 9.3             | 72            | 0.36   | 23.41 | 0.025 |
| 0 : 3 : 3                           | 5.11                           | 11.4            | 77            | 0.15   | 17.05 | 0.013 |
| 3 : 1.5 : 1.5                       | 4.23                           | 10.8            | 71            | 0.39   | 30.20 | 0.029 |
| 0 : 6 : 0                           | 4.52                           | 12.4            | 76            | 0.09   | 5.29  | 0.006 |
| 3 : 3 : 0                           | 3.38                           | 11.3            | 74            | 0.33   | 26.10 | 0.023 |

In the study of the physicomechanical properties of our sol–gel plates under uniaxial tension, it was found that deformation curves characteristic of plastic polymer materials which do not reach the yield point, e.g., xenopericardium or cartilaginous tissue, were recorded for all samples [12]. Plates based on AV and/or GM (no CS) show low elastoplastic properties in comparison with similar CS-containing compositions (Table 1). This indicates that CS makes a positive contribution to the formation of the structure of the plates with a high fraction of the elastic component of deformation. This behavior can be explained by the formation of a large number of intermolecular contacts between the components of the gel-forming mixture. This, in turn, leads to an increase in the number of physical nodes of the resulting network and contributes to the formation of a stronger and more elastic sol–gel plate.

The results of SEM microscopy of the solid phase of our sol–gel plates also showed a positive effect of the combined use of polysaccharides of different nature on the surface-morphological properties of the hybrid matrix. E.g., our analysis of SEM images revealed that the surface of all samples was represented by a non-porous structure with a small number of relatively uniform aggregates and structural inhomogeneities (Figure 2).
Figure 2. SEM images of the xerogel's morphostructure isolated from sol–gel plates based on polysaccharide component containing GM (a, b, d, e), AV (b, c, e, f) and CS (d–f).

The plates based on the neutral polysaccharide GM have a smooth morphostructure, those based on AV have a more granular one. It is worth noting that the joint presence of GM and AV enhances the structuring of the surface. For all the studied samples, the presence of the aminopolysaccharide CS in the composition contributes to the formation of a rougher surface relief.

Our studies have shown a significant effect of the polysaccharide’s nature on the morphological, sorption and elastoplastic properties of the sol–gel plates. According to SEM, the resulting material belongs to composites, AV and GM acts as a structure-forming component. The obtained structures can be used for the design of bioadhesive sensor coatings with a high therapeutic effect, which is an urgent area for theranostics and regenerative medicine.

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