Biodegradation Control of Chitosan Materials by Surface Modification with Copolymers of Glycidyl Methacrylate and Alkyl Methacrylates

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Abstract: Chitosan is a promising polymer from natural polysaccharides, which is an environmentally friendly compound from renewable raw materials. Chitosan has biodegradability, biocompatibility, and antibacterial and other activities. In this article, we report the biodegradation control of chitosan materials by use of random copolymers based on glycidyl methacrylate and (fluoro)alkyl methacrylates as surface modifiers. We show that grafting of copolymers allows increasing the hydrophobicity of chitosan materials with initial contact angles up to 114° from 89° for films and up to 154° from 123° for aerogels. We demonstrate that modified aerogels retain contact angles of more than 150° for a long contact time with water while the initial aerogel fully wets for 30 s. The resulting chitosan aerogels have high porosity with a pore size of 100-200 µm, and the pore walls are 0.6-0.7-µm-thick film formations. Our study of lyophilic properties of modified chitosan substrates showed a change in the hydrophobicity of the materials as a function of length of the hydrocarbon radical in the side groups of the (fluoro)alkyl methacrylates in the copolymers. We demonstrate that the rate of biodegradation of the resulting materials decreases with an increase in the number of hydrophobic groups in the modifier. The obtained chitosan materials with hydrophobic coatings have potential as a protective layer for wound dressings with an extended service life.

Keywords: Chitosan, Aerogel, Surface modification, Wettability, Biodegradability control

Introduction

Polysaccharides are well known in the development of wound dressings and other medical materials [1-3]. The most widespread polysaccharides on Earth include cellulose, chitin and its derivative chitosan, which are water-insoluble hydrophilic polymers [4] that swell in aqueous alkaline and saline solutions, thus causing loss of shape in products based on them [5]. Typically, the hydrophilicity of biopolymers accelerates their biodegradability in the presence of moisture due to the active reproduction of microorganisms in such an environment and the presence of enzymes and ions in water that affect the degradation kinetics. Therefore, it is necessary to control the hydrophilic and hydrophobic surface properties of such materials.

Since the late twentieth century, knowledge of the control of the lyophilic surface properties of materials has been actively developing [6-9]. A special place is held by the limit states of surface wetting with water, superhydrophilicity and superhydrophobicity, providing complete wettability or unwettability [10,11]. Targeted modification of the surface layer of materials changes the properties at the interface and makes it possible to impart oleophobic/oleophilic and other performance properties into the materials without changing the substrate properties as a whole, such as its biodegradability [12,13].

Recently, dressing materials have been actively used for burns and other injuries, which have a targeted effect and enhance the healing processes of wounds [1-3,14]. In addition to biodegradability, materials for tissue engineering should have biocompatibility, i.e., they should not cause a negative body response or biological potency [15,16]. In regenerative medicine, biodegradation of a polymer implant as an extracellular matrix for the attachment and growth of body tissue cells eliminates the need for its removal, which is accompanied by additional trauma. Consequently, at the end of the implant’s functional period, no surgical intervention is required to remove the implant after the growth of the person’s own tissues in that area [17-21]. Ideally, such a structure should have a certain decomposition rate, which can be controlled by the chemical structure of the material. The composition of the wound covering assumes the presence of an internal hydrophilic and wound-healing layer capable of absorbing all exudates produced by wounds. The outer layer must perform a protective function, i.e., it must have hydrophobicity that can be created by modification with compounds that have a low surface tension [22,23].

Therefore, one promising polymer is a natural polysaccharide, chitosan, which has properties, such as a film- and fiber-forming ability, biodegradability, biocompatibility, nontoxicity, and antimicrobial, antifungal, and other activities [1,24-28]. In addition, it represents an environmentally friendly compound from renewable raw materials.

Chitosan contains two types of functional groups: free amino groups and hydroxyl groups on C3 and C6 carbon atoms. Grafting of compounds interacting with the reaction centers of the chitosan allows the formation of functional derivatives. It is well known that chitosan is made hydrophobic mainly due to low molecular weight compounds that contain highly reactive groups. Among such modifiers

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are the known chlorosilanes [29,30], carbonyl compounds [31-35], anhydrides or acyl chlorides of aliphatic carboxylic acids [36,37] and haloalkanes [38] on the basis of hydrocarbons C10-C18 and others, which are capable of reacting with amino groups of the chitosan. In addition, there are modification approaches based on the electrostatic interaction and complexation of protonated amino group of chitosan with negatively charged polyanions [37,39] or fluorine-containing surfactants [40-42]. Unfortunately, poor mechanical and hydrophobic properties stability of obtained coatings, unsatisfied biodegradable of materials are often disadvantages of suggested pathways of chitosan modifications.

However, the modification of chitosan with synthetic polymers looks more promising in terms of the stability of the imparted properties, especially the lyophilic property [43-45]. The method includes preliminary synthesis of copolymers based on monomers with low surface tension and monomers with reactive groups and their subsequent reaction with complementary functional groups of the polysaccharide [46,47]. This modification can be carried out in two ways. The first involves dissolving chitosan in acetic or lactic acid with the addition of a modifying polymer dissolved in dioxane or tetrahydrofuran. The disadvantage of this approach is the formation of insoluble products, which complicates the formation of materials based on them [43, 48,49]. An alternative and the simplest and most promising method is surface modification of chitosan-based materials with copolymers containing oxirane groups that are capable of interacting with the amine and hydroxyl groups of chitosan upon heating [50-52]. In this work, we investigated the water-repellent properties of the polymer coatings based on random copolymers of alkyl methacrylates and glycidyl methacrylate on the surface of the film and aerogel chitosan materials for biodegradability control. Alkyl methacrylates ensure water-repelling properties, and glycidyl methacrylate acts as an anchor due to the presence of epoxide groups that are capable of interacting with amine and hydroxyl groups of the chitosan substrates.

This research aimed to elucidate the modification of chitosan-based materials with copolymers based on (fluoro)alkyl methacrylates and glycidyl methacrylate to control the lyophilic properties and biodegradability.

**Experimental**

**Materials**

Chitosan was from Bioprogress, Ltd. (Russia) (M=200 kDa, degree of deacetylation of 83 %, moisture content of 7 %); we also used glacial acetic acid (analytical grade, from Vekton, Russia), distilled water, aqueous ammonia (25 % aqueous solution, analytical grade, from Vekton, Russia), methanol (chemically pure, from Vekton, Russia), 25 % aqueous solution of glutaraldehyde (from Acros Organics), glycidyl methacrylate (GMA, 98 %, from Aldrich), hexyl methacrylate (HeMA, 97 %, from Aldrich), decyl methacrylate (DMA, 95 %, from Aldrich), lauryl methacrylate (LMA, 96 %, from Aldrich), stearyl methacrylate (SMA, 97 %, from Aldrich), 1,1,1,3,3,3-hexafluorisopropyl methacrylate (HFIM, 99 %, from Aldrich), methyl ethyl ketone (2-butanone, MEK, chemically pure, from Vekton, Russia), and azobisisobutyronitrile (AIBN, 98 %, from Aldrich).

**Preparation of Chitosan Materials**

Preparation of 2 % solutions of chitosan in 2 % acetic acid for the formation of the films was carried out according to prior procedures [31,53].

A 1 % solution of chitosan was prepared in 1 % aqueous acetic acid similarly to the film preparation procedure, followed by adding a 3 % aqueous solution of glutaraldehyde (the molar ratio of glutaraldehyde:chitosan was 1:1) [24]. The reaction mass was stirred with a magnetic stirrer for 30 min. The resulting gel was degassed in an ultrasonic bath at 37 kHz and 80 W for 10 min, placed in polypropylene molds, and left for 72 h at room temperature. Afterwards, the hydrogel was frozen for 12 h at -30 °C, followed by defrosting for 6 h at 25 °C. The gel was then transferred from the salt form to the basic form with an aqueous-alcoholic solution of ammonia (1:1 vol.) for 12 h. Further washing to a neutral medium was carried out with distilled water. The reduced hydrogels were frozen at -30 °C and then dried at -82±2 °C under vacuum in a 2.5-L FreeZone freeze dryer from Labconco Plus (USA).

The amount of reacted glutaraldehyde with chitosan was determined by the gravimetric method. The aerogel samples that contained the chitosan (0.1 g) were obtained with a molar ratio of amino group of chitosan:aldehyde group in glutaraldehyde of 1:1. The freeze-dried aerogels were weighted, and the amount of glutaraldehyde included in the material was found (~50-55 mol% from the initial amount of dialdehyde). Thus, the determined molar ratio of amino group of chitosan:aldehyde group of glutaraldehyde was 1:0.5, which indicates the content of free amino groups in the obtained chitosan aerogel was ~40 % (the initial degree of chitosan deacetylation was 83 %).

**Synthesis of Copolymers Based on Glycidyl Methacrylate and (fluoro)alkyl Methacrylates (poly(GMA-co-ALMA/FMA))**

The grafting to approach involves the preliminary synthesis of polymers, the functional groups of which react with complementary functional groups on the modified surface. The synthesis of random copolymers was carried out according to the free radical polymerization similar to the method described in ref. [54] with molar ratios for the GMA:FMA monomers of 1.0:2.2 and for the GMA:AIMA monomers of 4.0:1.0. The molecular weight characteristics of copolymers were described in ref. [46].
Modification of Chitosan-based Materials with Copolymers Based on Glycidyl Methacrylate and (fluoro)alkyl Methacrylates

Modification of polysaccharides (Figure 1) with a glycidyl methacrylate-based copolymer will yield a surface layer representing macromolecular chains of chitosan with randomly distributed branches of the graft copolymer formed as a result of the reaction between oxirane groups of glycidyl methacrylate and the functional (hydroxyl and amine) groups of chitosan.

The modification of chitosan-based materials was carried out by immersing test samples in a modified solution of poly(GMA-co-AlMA/FMA) in methyl ethyl ketone with a concentration of 3-7.5 wt.% for 60 min. Afterwards, the samples were removed from the solution and thermostated at 140 °C for 60 min. The ratio of the modified solution volume to the sample mass was 400, which was due to the high porosity of the samples (95-98 %). The samples were purified from unreacted copolymer in a Soxhlet apparatus using methyl ethyl ketone as the solvent.

The degree of grafting was determined gravimetrically as the ratio of the mass of the grafted copolymers to the mass of the initial chitosan aerogel material. The weight gain of the samples after grafting of copolymers and washing in a Soxhlet apparatus was ~ 4 %.

Methods

IR spectroscopy studies of the film chitosan materials were carried out using an InfraLUM FT-08 FTIR spectrometer (Russia).

The modifiers' effect on the structure, morphology, and surface texture of chitosan-based aerogels was investigated by scanning electron microscopy (SEM) using a Versa and Quanta 3D DualBeam apparatus from FEI (USA) at a voltage of 5 kV on a fractured surface of the sample obtained from the chitosan aerogel frozen in liquid nitrogen. The elemental composition was determined using an integrated EDAX Apollo X-SDD (USA) energy dispersive X-ray microanalysis system. The vapor pressure of water inside the chamber was 10-80 Pa.

The HLB (hydrophilic-lipophilic balance) value was calculated using the Davis method (formula (1)) [55]:

\[
HLB = 7 + \sum_{i=1}^{m} HLB_i - 0.475 \cdot n
\]  

(1)

where \( m \) is the number of hydrophilic groups in the molecule, \( HLB_i \) is the number for the \( i \)-th hydrophilic group, and \( n \) is the number of lipophilic groups in the molecule.

The contact angle (CA) was measured using an OCA 15EC apparatus (DataPhysics, Germany) according to the method described in ref. [54].

The drop behavior on the surface of spongy materials at long time intervals was studied in a chamber-in-chamber-type cell saturated with water vapor [56]. Thus, our contact angle measurements were carried out in accordance with the procedure described above.

Water absorption of the aerogels was estimated from the mass variation of samples following their placement in a container with distilled water. Before testing, the samples were oven dried at 102±2 °C until constant mass, which was used as the initial mass of the sample in the determination. The samples were immersed in vials with distilled water at a temperature of 25±3 °C. Before weighing, excess liquid was removed from the sample surface with filter paper, and the samples were immediately weighed. Subsequent measurements were carried out after 3, 24, 72, and 168 h from the beginning of the experiment.

The mass variation of the sample \( \Delta m, \text{g/g} \), was calculated using formula (2):

\[
\Delta m = \frac{m_i - m_0}{m_0}
\]  

(2)

where \( m_i \) is the mass of the sample after immersion, g; and \( m_0 \) is the mass of the sample before testing, g.

The arithmetic mean value of the three parallel experiments was taken as the result.

The thermal stabilities of the chitosan-based spongy materials were studied using a Q-1500D derivatograph of the Paulik-Paulik-Erdey system (Hungary) with a thermocouple during heating of the samples in ceramic crucibles from room temperature to 1000 °C in open air at a heating rate of 5 °C/min. The masses of the samples were 100-120 mg.

Biodegradability was studied using chitosan films in the form of 20×(3-4)-mm samples that were used as a substrate. The test samples were subjected to soil degradation. The soil was activated at a temperature of 20±5 °C for 30 days. During this period, the soil was stirred on a daily basis and moistened with distilled water every 48 h. The pH of the aqueous extract in the soil was determined before testing. The soil is considered fit for testing at pH 6-7.5. Afterwards, four 20×(3-4)-mm samples of unmodified chitosan films and four samples of each modified chitosan film were oven dried.
at 102±2 °C and weighed. The samples were then placed in a tray with activated soil in wells and dug in. The location of the films was marked with markers. The films were removed, washed in water, oven dried at 102±2 °C, and weighed every 15 days (up to 90 days) [57]. The arithmetic mean value of the four parallel experiments was taken as the result.

**Results and Discussion**

The surface modification of chitosan aerogels can be carried out using two methodologies: grafting from and grafting to/onto [6,7]. The first approach, grafting from, consists of polymerization of monomers on the initiator molecules attached to the carrier surface. As part of the grafting to/onto approach, the end groups of the pre-synthesized polymers react with complementary functional groups on the modified surface [58,59].

The copolymers based on glycidyl methacrylate and (fluoro)alkyl methacrylates interact with functional amine and hydroxyl groups of chitosan due to the presence of reactive oxirane groups in the composition according to the grafting to/onto approach. In this case, the aerogel surface layer will represent macromolecular chains of chitosan with randomly distributed branches of the graft copolymer (Figure 1). It was established in ref. [60] that this modification process is similar to the curing reactions of compounds that contain reactive epoxy groups. The interaction of amino and oxirane groups is carried out using the conditions of acid-base catalysis [60,61], with non-catalytic behavior also being possible at temperatures of 130-150 °C [62]. The glycidyl methacrylate-based copolymers were first dissolved in methyl ethyl ketone, and chitosan aerogels were immersed in the modifier solution. The most effective [46,47] concentration of the modified solution for obtaining superhydrophobic properties is 3 wt.%. The chitosan-based film materials were subjected to IR spectroscopy studies to confirm the grafting of the GMA- and AlMA-based copolymers. The IR spectra of the modified samples (Figure 2) were distinguished by the band at 1728 cm⁻¹. This peak corresponds to stretching vibrations of the carbonyl group in esters and was a consequence of the presence of poly(GMA-co-AlMA/FMA) graft copolymers on the chitosan film surface. The progress of the reaction in the amino group was evidenced by the reduction in intensity of the absorption band of NH₂ groups at 1584 cm⁻¹. Similar curves were obtained for other modifiers.

Poly(GMA-co-HFIM) was used as a modifier to determine the presence of graft copolymers in the bulk of the aerogel, which was due to the presence of an indicator fluorine atom in its composition. Based on the results of the X-ray microanalysis of the fracture area of the chitosan aerogel, fluorine was identified in the amount of 0.51 wt.% (Figure 3).

SEM images (Figure 4) show the morphology of aerogel fractures before and after modification. The resulting
chitosan aerogels have a high porosity with a pore size of 100-200 µm.

The pore walls were 600-700-nm-thick film formations (Figure 4c). The pore parameters were retained as a result of the modification; therefore, the pores were not filled with the modifying copolymer.

The modifiers selected for this study (Figure 1) can be ranked according to the increase in hydrophobicity subject to their hydrophilic-lipophilic balance (HLB) values (Table 1).

Based on the positive HLB values (Table 1) for the poly(GMA-co-HeMA) and poly(GMA-co-DMA) copolymers (2.025 and 0.125, respectively), it can be assumed that the hydrophobicity of the modified chitosan materials will either not change at all or will change only slightly at the initial instant of contact with water.

It is known from ref. [6] that the use of hydrophobic agents on smooth surfaces, such as films, enables contact angles no more than 120 °. Therefore, the hydrophobic properties of materials can be increased by the multilevel roughness of chitosan aerogels and further surface modification with GMA- and AlMA/FMA-based copolymers. The ratio of monomer units in the obtained copolymers is close to the theoretical molar ratio. Copolymers are characterized by a narrow molecular weight distribution and low molecular weights, while the close values of these parameters make it possible to compare their effect on hydrophobic properties in terms of their composition and structure [47,56]. Studies have shown (Figure 5) that grafting of poly(GMA-co-AlMA/FMA) copolymers onto the surface of chitosan films using 3 % modified solutions allows to attain hydrophobicity characterized by contact angles of up to 114 °. Regarding aerogels, treatment with GMA- and AlMA/FMA-based
copolymers allows a superhydrophobic state with contact angles up to 154°.

One of the main stability characteristics of superhydrophobic properties is the preservation of the wetting regime at prolonged contact between the droplet and the coating in an atmosphere saturated with water vapor. The resulting coatings based on GMA- and AIMA/FMA-based copolymers exhibit a stable high and superhydrophobic state (Figure 6). Figure 6 shows that the unmodified aerogel completely absorbed a water drop after 30 s of contact, while the aerogel modified with the copolymer poly(GMA-co-LMA) retained a contact angle of approximately 150° for a long time. However, the contact angles remained unchanged with an increase in modifier concentration, which indicated preservation of the porous structure of the aerogels.

As shown in Figures 6 and 7, the unmodified chitosan aerogel samples showed high absorption capacity, and the water absorption value was 18.92 g/g (Figure 7), which was explained by the presence of hydrophilic groups (-OH, -NH₂) in the chitosan.

Modification of the aerogel samples with a poly(GMA-co-HeMA) copolymer led to a significant degradation and decrease in water absorption, which was linearly dependent on the copolymer concentration in the modified solution. The alkyl substituent in the modifier provided the surface with hydrophobic properties due to the displacement of the hydrogen atom in the hydrophilic amino and hydroxyl groups of chitosan and their shielding.

Because all materials used as wound dressings must be autoclaved at a temperature of 200 °C or higher, it is necessary to study the thermal stability of the resulting aerogels. Figure 8 shows the results of the thermogravimetric analysis (TG and DTG curves).

**Figure 6.** Dependences of the contact angle for a distilled water droplet on the time of contact with surfaces of the initial chitosan aerogel (1) and chitosan aerogel modified with a solution of copolymers: poly(GMA-co-HeMA) at 6 wt.% (2) and 7.5 wt.% (3) and poly(GMA-co-LMA) at 6 wt.% (4) and 7.5 wt.% (5).

**Figure 7.** Dependence of water absorption on the poly(GMA-co-HeMA) copolymer concentration in the modified solution.

**Figure 8.** Weight loss curves (TG) and differential thermogravimetry curves (DTG) for the unmodified chitosan film (1) and aerogel (2); aerogels modified with copolymers: poly(GMA-co-HeMA) (3) and poly(GMA-co-LMA) (4).
As shown in Figure 8 (TG), the weight loss of the samples in the temperature range up to 600 °C occurred in several stages. The mass variation in the temperature range up to 200-240 °C was due to the desorption of moisture from the surface of the samples and from the bulk as a result of breakdown of hydrogen bonds between the water molecules and polar functional groups of chitosan.

The sample decomposition rate was the highest in the temperature range of 240-300 °C (Figure 8, DTG). For the chitosan-based film samples, the rate of weight loss (the maximum decomposition rate) in this range determined from the variation in the peak intensity was 7.2 %/min. Moreover, for aerogels, i.e., chitosans cross-linked with glutaraldehyde, namely, samples 2, 3, and 4, the rate of weight loss was two times less at 3.5 %/min. Thus, the decomposition rate of aerogel materials was lower than that of the chitosan film. The weight loss for all samples was approximately 60 % of the initial weight (Figure 8, TG).

The final stage of decomposition occurred in the temperature range from 300 to 600 °C with the formation of coke residue. Thus, the decomposition temperature of the resulting samples corresponded to ~250 °C, i.e., chitosan-based hydrophobic materials meet the thermal stability criteria.

To study the effect of the lyophilicity of the film materials on the biodegradation time, the samples were subjected to in vitro soil degradation. The study of the decomposition of the chitosan films showed (Figure 9) that the initial chitosan samples with a contact angle of 86±3 ° showed 90 % soil biodegradation within 80-90 days. The weight loss of the samples treated with GMA- and AlMA/FMA-based copolymers with contact angles of 110-120 ° was 5-10 %. This suggests the possibility of decreasing the rate of decomposition of the polysaccharide film materials by modification with GMA- and AlMA/FMA-based copolymers.

According to Figure 9a, the increase in the size of the hydrocarbon radical in the modifying copolymer to C<sub>12</sub>, as well as the presence of a fluoroalkyl radical, maximally reduced the rate of decomposition of the resulting materials. This can be explained by the use of long hydrophobic alky substituents of the modifying copolymers for shielding of the hydrophilic amine and hydroxyl groups of chitosan. The dependence of the decomposition rate on the length of the hydrocarbon substituent of the modifier (Figure 9b) corresponds to the HLB values provided in Table 1. However, the rate of decomposition of chitosan-based materials modified with a poly(GMA-co-SMA) copolymer did not correlate with the size of the hydrocarbon substituent (C<sub>18</sub>). This may be due to the association of long hydrophobic tails of SMA units, which increased the availability of hydrophilic groups of chitosan for interaction with water molecules. This result is in line with a previous publication [46], which showed that given comparable molecular weights, the poly(GMA-co-LMA) copolymer has large macromolecular tangles in comparison with poly(GMA-co-SMA).

**Conclusion**

In this paper, we first proposed the use of random copolymers based on glycidyl methacrylate and alkyl or fluoroalkyl methacrylates as wettability and biodegradability regulators for chitosan-based films and aerogels. Chitosan-based materials were obtained with an adjustable level of hydrophilic, hydrophobic, and operational characteristics: the water contact angle was up to ~114 ° for films and up to ~154 ° for aerogels, and the water absorption was less than 1 g/g. The effect of the chitosan surface modification on the
possibility of changing the biodegradation rate by imparting hydrophobic properties was revealed, which leads to the prolonged action of the materials in a humid environment. Thus, it takes unmodified chitosan-based films approximately 90 days to decompose completely, which is in contrast to those modified with copolymers based on glycidyl methacrylate and (fluoro)alkyl methacrylates, which decompose by 5-10 wt.% as a function of the length of the modifier’s hydrocarbon radical during the same period.

The complex of lyophilic characteristics of the obtained chitosan films and aerogels resulting from the modification are a prerequisite for further study of the operational, microbiological, and toxic properties of these materials from the perspective of their potential use as wound dressings with an extended service life.

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**Conflicts of Interest**

The authors declare that they have no conflict of interest.

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