

Biodegradation Control of Chitosan Materials By Surface Modification With Copolymers of Glycidyl Methacrylate and Alkyl Methacrylates

Evgeny Bryuzgin (✉ bryuzgin_e@mail.ru)

Volgograd State Technical University: Volgogradskij gosudarstvennyj tehničeskij universitet
<https://orcid.org/0000-0002-2930-1910>

Ekaterina Bryuzgina

Volgograd State Technical University: Volgogradskij gosudarstvennyj tehničeskij universitet

Vitaliya Yartseva

Volgograd State Technical University: Volgogradskij gosudarstvennyj tehničeskij universitet

Kristina Belina

Volgograd State Technical University: Volgogradskij gosudarstvennyj tehničeskij universitet

Olga Makevnina

Volgograd State Technical University: Volgogradskij gosudarstvennyj tehničeskij universitet

Olga Kolyaganova

Volgograd State Technical University: Volgogradskij gosudarstvennyj tehničeskij universitet

Victor Klimov

Volgograd State Technical University: Volgogradskij gosudarstvennyj tehničeskij universitet

Alexander Navrotskiy

Volgograd State Technical University: Volgogradskij gosudarstvennyj tehničeskij universitet

Ivan Novakov

Volgograd State Technical University: Volgogradskij gosudarstvennyj tehničeskij universitet

Research Article

Keywords: chitosan, aerogel, surface modification, wettability, biodegradability control

Posted Date: April 16th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-396386/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Chitosan is one of promising polymer from natural polysaccharides, which is an environmentally friendly compound from renewable raw materials. Chitosan has biodegradability, biocompatibility, and exhibits antimicrobial, antibacterial, and other activities. In this article, we report the first use of copolymers based on glycidyl methacrylate and (fluoro)alkyl methacrylates as material surface wettability modifiers based on a chitosan, and we show that grafting of copolymers allows an increase in the hydrophobicity of films with contact angles up to 114° and up to 154° for aerogels. The resulting chitosan aerogels have high porosity with a pore size of $100\text{--}200\ \mu\text{m}$ and the pore walls are $0.6\text{--}0.7\ \mu\text{m}$ -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 (fluoro)alkyl methacrylates in the copolymers. Additionally, the rate of biodegradation of the resulting materials decreased with an increase in the number of hydrophobic groups in the modifier. Obtained chitosan materials with hydrophobic coatings have potential as a protective layer for wound dressings with an extended service life.

Introduction

The advancement of modern medical technologies requires the use of biodegradable polymer and composite materials and products. 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 (C. M. Da Silva et al., 2011; Hong et al., 2008; Muzzarelli et al., 1993; Y. Wan et al., 2007; Ying Wan et al., 2006; Y. Wang et al., 2019). Ideally, such a structure should have a certain decomposition rate, which can be controlled by the chemical structure of the material.

Since the late twentieth century, the knowledge of the control of lyophilic surface properties of materials has been actively developing (Boinovich & Emelyanenko, 2008; Evgeny Bryuzgin et al., 2020; Evgeniy V. Bryuzgin et al., 2017; Zdyrko & Luzinov, 2011). A special place is held by the limit states of surface wetting with water, superhydrophilicity and superhydrophobicity, providing complete wettability or unwettability (Bhushan & Jung, 2011; Teas et al., 2001). 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 the materials without changing the substrate properties as a whole, such as its biodegradability (Nevestenko et al., 2020; Xu et al., 2015).

In addition to biodegradability, materials for tissue engineering should have biocompatibility, i.e., they should not cause a negative body response or biological potency (D. da Silva et al., 2018; Wu et al., 2005). Recently, dressing materials have been actively used for burns and other injuries, which have a targeted effect and enhance the healing processes of wounds (Ishihara et al., 2002; Montes & Maleki, 2020; Quignard et al., 2008; Zhang et al., 2020). 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 having a low surface tension.

Polysaccharides are water-insoluble hydrophilic polymers that swell in aqueous alkaline and saline solutions, thus causing loss of shape in products based on them (Ganesan et al., 2018; İlk et al., 2020). It is common knowledge that 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.

Thus, one promising polymer is a natural polysaccharide, chitosan, which is an environmentally friendly compound from renewable raw materials. It has properties, such as film- and fiber-forming ability, biodegradability, and biocompatibility, and exhibits antimicrobial, antibacterial, and other activities (Agnihotri et al., 2004; Fernandez-Saiz et al., 2009; Ishihara et al., 2002; Wei et al., 2020).

Chitosan contains two types of functional groups: free amino groups and hydroxyl groups based on C3 and C6 carbon atoms. Grafting of compounds interacting with the reaction centers of the polysaccharide allows the formation of functional derivatives. Chitosan is made hydrophobic mainly due to low molecular weight compounds containing highly reactive groups. Among such modifiers are the known anhydrides or acyl chlorides of aliphatic carboxylic acids (Höhne et al., 2007), chlorosilanes (W. Song et al., 2010; Su et al., 2017), and carbonyl compounds (Chernyshova et al., 2017; Takeshita et al., 2017), which are capable of reacting with amino groups of the polysaccharide. In addition, there are modification approaches based on the electrostatic interaction of the amino group of chitosan with a negatively charged anion (S. Wang et al., 2018), for example, fluorine-containing surfactants (N. A. Ivanova & Philipchenko, 2012; Nina A. Ivanova et al., 2013; K. Song et al., 2015).

However, the modification of chitosan with synthetic polymers looks more promising in terms of the stability of the imparted properties. The method consists in 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 (Evgeny Bryuzgin et al., 2020; Evgeniy V. Bryuzgin et al., 2017). This modification can be carried out in two ways. The first involves dissolving chitosan in acetic or lactic acid with the addition of a 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. 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 amine and hydroxyl groups of chitosan upon heating.

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

2.1. Materials

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

2.2. Preparation of a 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 (Chernyshova et al., 2017; Yudin et al., 2014).

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) (Wei et al., 2020). The reaction mass was stirred with a magnetic stirrer for 30 min. The resulting gel was degassed in an ultrasonic bath 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 $-82\pm 2^{\circ}\text{C}$ under vacuum in a 2.5-L FreeZone freeze dryer from Labconco plus (USA).

2.3. Synthesis of copolymers based on glycidyl methacrylate and (fluoro)alkyl methacrylates (poly(GMA-co-AIMA/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. (Klimov et al., 2016) with molar ratios for the GMA:FMA monomers = 1.0:2.2 and GMA:AIMA monomers = 4.0:1.0. The molecular weight characteristics of copolymers were described in ref. (Evgeny Bryuzgin et al., 2020)

2.4. 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-AIMA/FMA) in methyl ethyl ketone with a concentration of 3 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 cu, 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.

2.5. Methods

The 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)) (Davies, 1957):

$$HLB = 7 + \sum_{i=1}^m HLB_i - 0,475 \cdot n \quad (1)$$

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. (Klimov et al., 2016).

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 (Evgeny V. Bryuzgin et al., 2017). 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 $102 \pm 2^\circ\text{C}$ 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 $25 \pm 3^\circ\text{C}$. 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 Δm , g/g, was calculated using Formula (2):

$$\Delta m = \frac{m_i - m_0}{m_0}, \quad (2)$$

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 test result.

The thermal stability of the chitosan-based spongy materials was 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 mass of the samples was 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 and four samples of each modified chitosan films were oven dried at 102±2°C and weighed at a time. The samples were then placed in a tray with activated soil in wells and digged 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) (Calmon-Decriaud et al., 1998).

Discussion

The surface modification of chitosan aerogels can be carried out in two methodologies: “grafting from” and “grafting to/onto” (Boinovich & Emelyanenko, 2008; Zdyrko & Luzinov, 2011). The first approach, “grafting from”, consists of the 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 (Hadjichristidis, 2002; Mochalova et al., 2006).

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. In this case, the aerogel surface layer will represent macromolecular chains of chitosan with

randomly distributed branches of the graft copolymer (Figure 1). It has been established in ref. (Tanaka & Kakiuchi, 1963) that this modification process is mechanically 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 (Tanaka & Kakiuchi, 1963, 1964), with non-catalytic behavior also being possible at temperatures of 130–150°C (Galy J., Sabra A., 1986). The glycidyl methacrylate-based copolymers were previously dissolved in methyl ethyl ketone, and chitosan aerogels were immersed in the modifier solution. The most effective (Evgeny Bryuzgin et al., 2020; Evgeny V. Bryuzgin et al., 2017) concentration of the modified solution for obtaining superhydrophobic properties is 3 wt.%.

Chitosan-based film materials were subjected to IR spectroscopy studies to confirm the grafting of the GMA- and AIMA-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-AIMA/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 NH_2 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 high porosity with a pore size of 100–200 μm .

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

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

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

It is known from ref. (Boinovich & Emelyanenko, 2008) that the use of hydrophobic agents on smooth surfaces, such as films, enables achievement of 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 AIMA/FMA-based copolymers. Studies have shown (Figure 5) that grafting of poly(GMA-co-AIMA/FMA) copolymers onto the surface of chitosan films using 3% modified solutions allows hydrophobicity characterized by contact angles up to 114° . Regarding

aerogels, treatment with GMA- and AIMA/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 the GMA- and AIMA/FMA-based copolymers exhibit a stable high and superhydrophobic state (Figure 6). The figure shows that the unmodified aerogel completely absorbed a water drop after 30 s of contact, while the aerogel modified with GMA-LMA copolymer 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 the 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 and 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).

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 spongy materials was lower than that of the chitosan film.

The final stage of decomposition occurred in the temperature range from 300 to 600°C with the formation of coke residue. The weight loss for all samples was approximately 60% of the initial weight (Figure 8, TG). 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 $86\pm 3^\circ$ showed 90% soil biodegradation within 80–90 days. The weight loss of the samples treated with GMA- and AIMA/FMA-based copolymers with contact angles of $110\text{--}120^\circ$ was 5–10%. This suggests the possibility of decreasing the rate of decomposition of the polysaccharide film materials by modification with GMA- and AIMA/FMA-based copolymers.

According to Figure 9a, the increase in the size of the hydrocarbon radical in the modifying copolymer to C_{12} , 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 alkyl substituents of the modifying copolymers for shielding of 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_{18}). 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 (Evgeny Bryuzgin et al., 2020), which showed that given comparable molecular weights, the poly(GMA-co-LMA) copolymer has large macromolecular coils in comparison with poly(GMA-co-CMA).

Conclusion

In this paper, we first proposed the use of copolymers based on glycidyl methacrylate and alkyl or fluoroalkyl methacrylates as wettability regulators for chitosan-based films and aerogels. Chitosan-based materials were obtained with an adjustable level of hydrophilic and hydrophobic (contact angle up to $\sim 114^\circ$ for films and up to $\sim 154^\circ$ for aerogels) and operational characteristics (water absorption 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, and it leads to the prolonged action of 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.

The complex lyophilic characteristics of 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.

Declarations

Funding

We acknowledge funding from the Ministry of Science and Higher Education of the Russian Federation (*Agreement No. 075-15-2020-794*).

Acknowledgements

The authors would like to thank Falcon Scientific Editing (<https://falconediting.com>) for proofreading the English language in this paper.

Conflicts of interest/Competing interests

The authors declare that they have no conflict of interest.

Availability of data and material

Not applicable

Code availability

Not applicable

Authors' contributions

Conceptualization: Evgeny Bryuzgin, Ekaterina Bryuzgina

Formal analysis and investigation: Ekaterina Bryuzgina, Vitaliya Yartseva, Olga Makevnina, Kristina Belina, Olga Kolyaganova, Viktor Klimov

Writing - original draft preparation: Ekaterina Bryuzgina

Resources: Evgeny Bryuzgin, Viktor Klimov

Writing - Review and Editing: Ivan Novakov, Alexander Navrotskiy, Evgeny Bryuzgin

Project administration: Alexander Navrotskiy

Supervision: Ivan Novakov

Funding acquisition: Ivan Novakov

Ethics approval

Not applicable

Consent to participate

Not applicable

Consent for publication

Not applicable

References

1. Agnihotri SA, Mallikarjuna NN, Aminabhavi TM (2004) Recent advances on chitosan-based micro- and nanoparticles in drug delivery. *J Controlled Release* 100(1):5–28. <https://doi.org/10.1016/j.jconrel.2004.08.010>
2. Bhushan B, Jung YC (2011) Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction. *Prog Mater Sci* 56(1):1–108. <https://doi.org/10.1016/j.pmatsci.2010.04.003>
3. Boinovich LB, Emelyanenko AM (2008) Hydrophobic materials and coatings: principles of design, properties and applications. *Rus Chem Rev* 77(7):583–600. <https://doi.org/10.1070/rc2008v077n07abeh003775>
4. Bryuzgin E, Klimov V, Le MD, Navrotskiy A, Novakov I (2020) The Superhydrophobic State Stability of Coatings Based on Copolymers of Glycidyl Methacrylate and Alkyl Methacrylates on Cotton Fabric Surface. *Fibers Polym* 21(5):1032–1038. <https://doi.org/10.1007/s12221-020-9741-y>
5. Bryuzgin EV, Klimov VV, Le MD, Nguyen TH, Navrotskiy AV, Novakov IA (2017) Superhydrophobic behavior of lauryl methacrylate copolymers on the cotton fabric surface. *Surface Innovations* 5(3):147–153. <https://doi.org/10.1680/jsuin.17.00012>
6. Bryuzgin EV, Klimov VV, Repin SA, Navrotskiy AV, Novakov IA (2017) Aluminum surface modification with fluoroalkyl methacrylate-based copolymers to attain superhydrophobic properties. *Appl Surf Sci* 419:454–459. <https://doi.org/10.1016/j.apsusc.2017.04.222>
7. Calmon-Decriaud A, Bellon-Maurel V, Silvestre F (1998) Standard methods for testing the aerobic biodegradation of polymeric materials. Review and perspectives. *Blockcopolymers-Polyelectrolytes-Biodegradation* 135:207–226
8. Chernyshova EB, Berezin AS, Tuzhikov OI (2017) Hydrophobization of chitosan-based films with acrolein. *Russ J Appl Chem* 90(7):1165–1170. <https://doi.org/10.1134/S1070427217070229>
9. Da Silva CM, Silva D, Modolo DL, Alves LV, De Resende RB, Martins MA, C. V. B., & De, Fátima, Â (2011) Schiff bases: A short review of their antimicrobial activities. *Journal of Advanced Research*, 2(1), 1–8. <https://doi.org/10.1016/j.jare.2010.05.004>
10. da Silva D, Kaduri M, Poley M, Adir O, Krinsky N, Shainsky-Roitman J, Schroeder A (2018) Biocompatibility, biodegradation and excretion of polylactic acid (PLA) in medical implants and theranostic systems. *Chem Eng J* 340:9–14. <https://doi.org/10.1016/j.cej.2018.01.010>
11. Davies JT (1957) A quantitative kinetic theory of emulsion type. I. Physical chemistry of the emulsifying agent. *A quantitative Kinetic Theory of Emulsion Type I Physical Chemistry the Emulsifying Agent* 1(1):426–438

12. Fernandez-Saiz P, Lagarón JM, Ocio MJ (2009) Optimization of the film-forming and storage conditions of chitosan as an antimicrobial agent. *J Agric Food Chem* 57(8):3298–3307. <https://doi.org/10.1021/jf8037709>
13. Galy J, Sabra A, P. J. P (1986) Characterization of epoxy thermosetting systems by differential scanning calorimetry. *Polym Eng Sci* 26(21):1514–1523. <https://doi.org/10.3139/9781569906446.007>
14. Ganesan K, Budtova T, Ratke L, Gurikov P, Baudron V, Preibisch I, Niemeyer P, Smirnova I, Milow B (2018) Review on the production of polysaccharide aerogel particles. *Materials* 11(11):2144–2181. <https://doi.org/10.3390/ma11112144>
15. Hadjichristidis N (2002) Graft copolymers. *Encyclopedia of Polymer Science Technology* 6:38. [https://doi.org/10.1016/s0958-2118\(02\)80180-x](https://doi.org/10.1016/s0958-2118(02)80180-x)
16. Höhne S, Frenzel R, Heppe A, Simon F (2007) Hydrophobic chitosan microparticles: Heterogeneous phase reaction of chitosan with hydrophobic carbonyl reagents. *Biomacromol* 8(7):2051–2058. <https://doi.org/10.1021/bm0702354>
17. Hong Y, Gong Y, Gao C, Shen J (2008) Collagen-coated polylactide microcarriers/chitosan hydrogel composite: Injectable scaffold for cartilage regeneration. *J Journal of Biomedical Materials Research Part A: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials*, 85(3), 628–637. <https://doi.org/10.1002/jbm.a.31603>
18. İlk S, Ramanauskaitė A, Koç Bilican B, Mulerčikas P, Çam D, Onses MS, Torun I, Kazlauskaitė S, Baublys V, Aydın Ö, Zang LS, Kaya M (2020) Usage of natural chitosan membrane obtained from insect corneal lenses as a drug carrier and its potential for point of care tests. *Materials Science Engineering: C Engineering C* 112:110897. <https://doi.org/10.1016/j.msec.2020.110897>
19. Ishihara M, Nakanishi K, Ono K, Sato M, Kikuchi M, Saito Y, Yura H, Matsui T, Hattori H, Uenoyama M, Kurita A (2002) Photocrosslinkable chitosan as a dressing for wound occlusion and accelerator in healing process. *Biomaterials* 23(3):833–840. [https://doi.org/10.1016/S0142-9612\(01\)00189-2](https://doi.org/10.1016/S0142-9612(01)00189-2)
20. Ivanova NA, Philipchenko AB (2012) Superhydrophobic chitosan-based coatings for textile processing. *Appl Surf Sci* 263:783–787. <https://doi.org/10.1016/j.apsusc.2012.09.173>
21. Ivanova NA, Rutberg GI, Philipchenko AB (2013) Enhancing the superhydrophobic state stability of chitosan-based coatings for textiles. *Macromol Chem Phys* 214(13):1515–1521. <https://doi.org/10.1002/macp.201300273>
22. Klimov VV, Bryuzgin EV, Le MD, Zelenova EA, Nguyen TH, Navrotskii AV, Nishide H, Novakov IA (2016) An investigation of the hydrophobic property stability of grafted polymeric coatings on a cellulose material surface. *Polymer Science - Series D* 9(4):364–367. <https://doi.org/10.1134/S1995421216040080>
23. Mochalova AE, Zaborshchikova NV, Knyazev AA, Smirnova LA, Izvozchikova VA, Medvedeva VV, Semchikov YD (2006) Graft polymerization of acrylamide on chitosan: Copolymer structure and

- properties. *Polymer Science - Series A* 48(9):918–923.
<https://doi.org/10.1134/S0965545X06090069>
24. Montes S, Maleki H (2020) Aerogels and their applications. *Colloidal Metal Oxide Nanoparticles*, 337–399. <https://doi.org/10.1016/b978-0-12-813357-6.00015-2>
 25. Muzzarelli RAA, Biagini G, Bellardini M, Simonelli L, Castaldini C, Fratto G (1993) Osteoconduction exerted by methylpyrrolidinone chitosan used in dental surgery. *Biomaterials* 14(1):39–43.
[https://doi.org/10.1016/0142-9612\(93\)90073-B](https://doi.org/10.1016/0142-9612(93)90073-B)
 26. Nevestenko MA, Bryuzgina EB, Tuzhikov OI, Bryuzgin EV, Tarasova YS (2020) Study of Properties of Film Materials Based on Cellulose and Polyurethane Rubbers for Drainage of Oils. *Russ J Appl Chem* 93(4):556–563. <https://doi.org/10.1134/S1070427220040114>
 27. Quignard F, Valentin R, Di Renzo F (2008) Aerogel materials from marine polysaccharides. *New J Chem* 32(8):1300–1310. <https://doi.org/10.1039/b808218a>
 28. Song K, Gao A, Cheng X, Xie K (2015) Preparation of the superhydrophobic nano-hybrid membrane containing carbon nanotube based on chitosan and its antibacterial activity. *Carbohydr Polym* 130:381–387. <https://doi.org/10.1016/j.carbpol.2015.05.023>
 29. Song W, Gaware VS, Rúnarsson ÖV, Másson M, Mano JF (2010) Functionalized superhydrophobic biomimetic chitosan-based films. *Carbohydr Polym* 81(1):140–144.
<https://doi.org/10.1016/j.carbpol.2010.01.041>
 30. Su C, Yang H, Zhao H, Liu Y, Chen R (2017) Recyclable and biodegradable superhydrophobic and superoleophilic chitosan sponge for the effective removal of oily pollutants from water. *Chem Eng J* 330:423–432. <https://doi.org/10.1016/j.cej.2017.07.157>
 31. Takeshita S, Konishi A, Takebayashi Y, Yoda S, Otake K (2017) Aldehyde Approach to Hydrophobic Modification of Chitosan Aerogels. *Biomacromol* 18(7):2172–2178.
<https://doi.org/10.1021/acs.biomac.7b00562>
 32. Tanaka Y, Kakiuchi H (1963) Study of epoxy compounds. Part I. Curing reactions of epoxy resin and acid anhydride with amine and alcohol as catalyst. *J Appl Polym Sci* 7(3):1063–1081.
<https://doi.org/10.1002/app.1963.070070322>
 33. Tanaka Y, Kakiuchi H (1964) Study of epoxy compounds. Part VI. Curing reactions of epoxy resin and acid anhydride with amine, acid, alcohol, and phenol as catalysts. *Journal of Polymer Science Part A: General Papers* 2(8):3405–3430. <https://doi.org/10.1002/pol.1964.100020804>
 34. Teas C, Kalligeros S, Zanicos F, Stournas S, Lois E, Anastopoulos G (2001) Investigation of the effectiveness of absorbent materials in oil spills clean up. *Desalination* 140(3):259–264.
[https://doi.org/10.1016/S0011-9164\(01\)00375-7](https://doi.org/10.1016/S0011-9164(01)00375-7)
 35. Wan Y, Fang Y, Wu H, Cao X (2007) Porous polylactide/chitosan scaffolds for tissue engineering. *Journal of Biomedical Materials Research Part A* 80(4):776–789
 36. Wan Y, Wu H, Yu A, Wen D (2006) Biodegradable polylactide/chitosan blend membranes. *Biomacromol* 7(4):1362–1372. <https://doi.org/10.1021/bm0600825>

37. Wang S, Sha J, Wang W, Qin C, Li W, Qin C (2018) Superhydrophobic surfaces generated by one-pot spray-coating of chitosan-based nanoparticles. *Carbohyd Polym* 195:39–44. <https://doi.org/10.1016/j.carbpol.2018.04.068>
38. Wang Y, Su Y, Wang W, Fang Y, Riffat SB, Jiang F (2019) The advances of polysaccharide-based aerogels: Preparation and potential application. *Carbohyd Polym*, 115242. <https://doi.org/10.1016/j.carbpol.2019.115242>
39. Wei S, Ching YC, Chuah CH (2020) Synthesis of chitosan aerogels as promising carriers for drug delivery: A review. *Carbohyd Polym* 231:115744. <https://doi.org/10.1016/j.carbpol.2019.115744>
40. Wu T, Zivanovic S, Draughon FA, Conway WS, Sams CE (2005) Physicochemical properties and bioactivity of fungal chitin and chitosan. *J Agric Food Chem* 53(10):3888–3894. <https://doi.org/10.1021/jf048202s>
41. Xu Z, Zhao Y, Wang H, Wang X, Lin T (2015) A superamphiphobic coating with an ammonia - triggered transition to superhydrophilic and superoleophobic for oil–water separation. *Angew Chem Int Ed* 54(15):4527–4530. <https://doi.org/10.1002/anie.201411283>
42. Yudin VE, Dobrovolskaya IP, Neelov IM, Dresvyanina EN, Popryadukhin PV, Ivan’Kova EM, Elokhovskii VY, Kasatkin IA, Okrugin BM, Morganti P (2014) Wet spinning of fibers made of chitosan and chitin nanofibrils. *Carbohyd Polym* 108(1):176–182. <https://doi.org/10.1016/j.carbpol.2014.02.090>
43. Zdyrko B, Luzinov I (2011) Polymer brushes by the “grafting to” method. *Macromol Rapid Commun* 32(12):859–869. <https://doi.org/10.1002/marc.201100162>
44. Zhang G, Zheng G, Ren T, Zeng X, van der Heide E (2020) Dopamine hydrochloride and carboxymethyl chitosan coatings for multifilament surgical suture and their influence on friction during sliding contact with skin substitute. *Friction* 8(1):58–69. <https://doi.org/10.1007/s40544-018-0242-6>

Tables

Table 1 HLB (hydrophilic-lipophilic balance) values of poly(GMA-co-AIMA/FMA) copolymers subject to molar ratios

Polymer	Structure of the hydrocarbon substituent in the methacrylate' monomer unit	Molar ratio of monomers in the copolymer	HLB, cu
poly(GMA-co-HeMA)	$-(\text{CH}_2)_5\text{-CH}_3$	4.0/1.0	2.025
poly(GMA-co-DMA)	$-(\text{CH}_2)_9\text{-CH}_3$	4.0/1.0	0.125
poly(GMA-co-LMA)	$-(\text{CH}_2)_{11}\text{-CH}_3$	4.0/1.0	-1.775
poly(GMA-co-SMA)	$-(\text{CH}_2)_{17}\text{-CH}_3$	4.0/1.0	-3.675
poly(GMA-co-HFIM)	$-\text{CH}(\text{CF}_3)_2$	1.0/2.2	-5.235

Figures

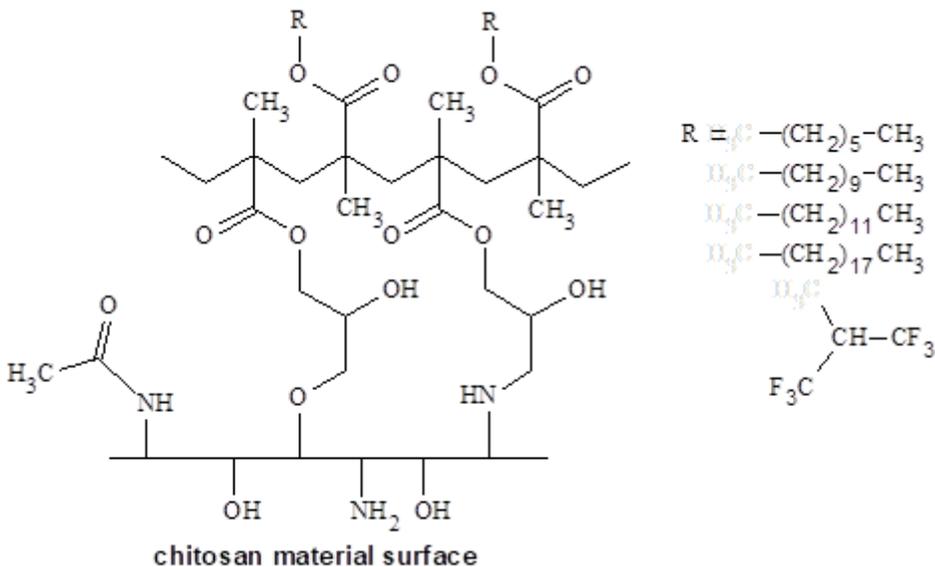


Figure 1

Structure of chitosan-based material modified with poly(GMA-co-AIMA/FMA) copolymers

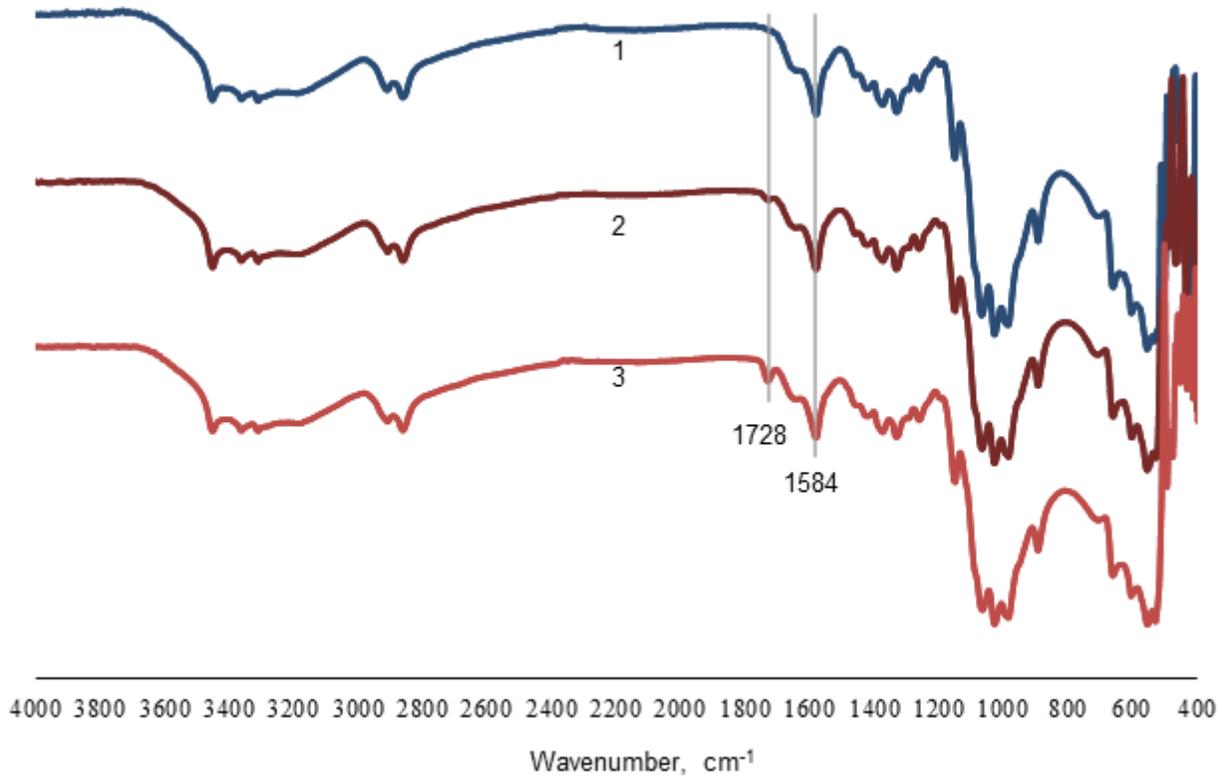


Figure 2

IR spectra of the initial chitosan film (1) and chitosan film modified with 4.5% solution of poly(GMA-co-HeMA) (2); 4.5% solution of poly(GMA-co-LMA) (3), following Soxhlet extraction

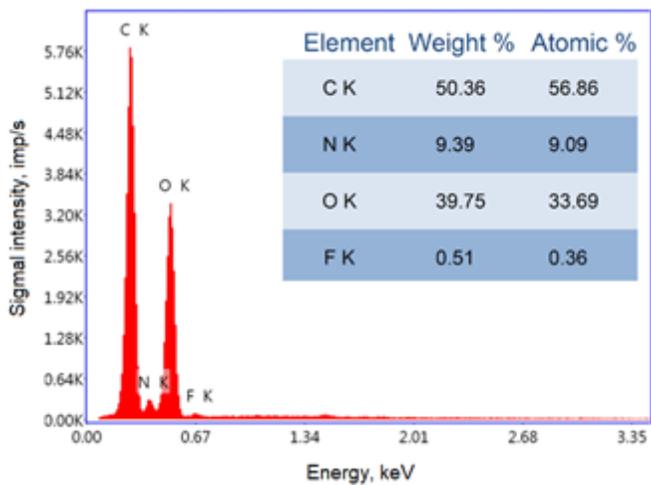


Figure 3

X-ray microanalysis of the fracture of the chitosan aerogel modified with a poly(GMA-co-HFIM) copolymer

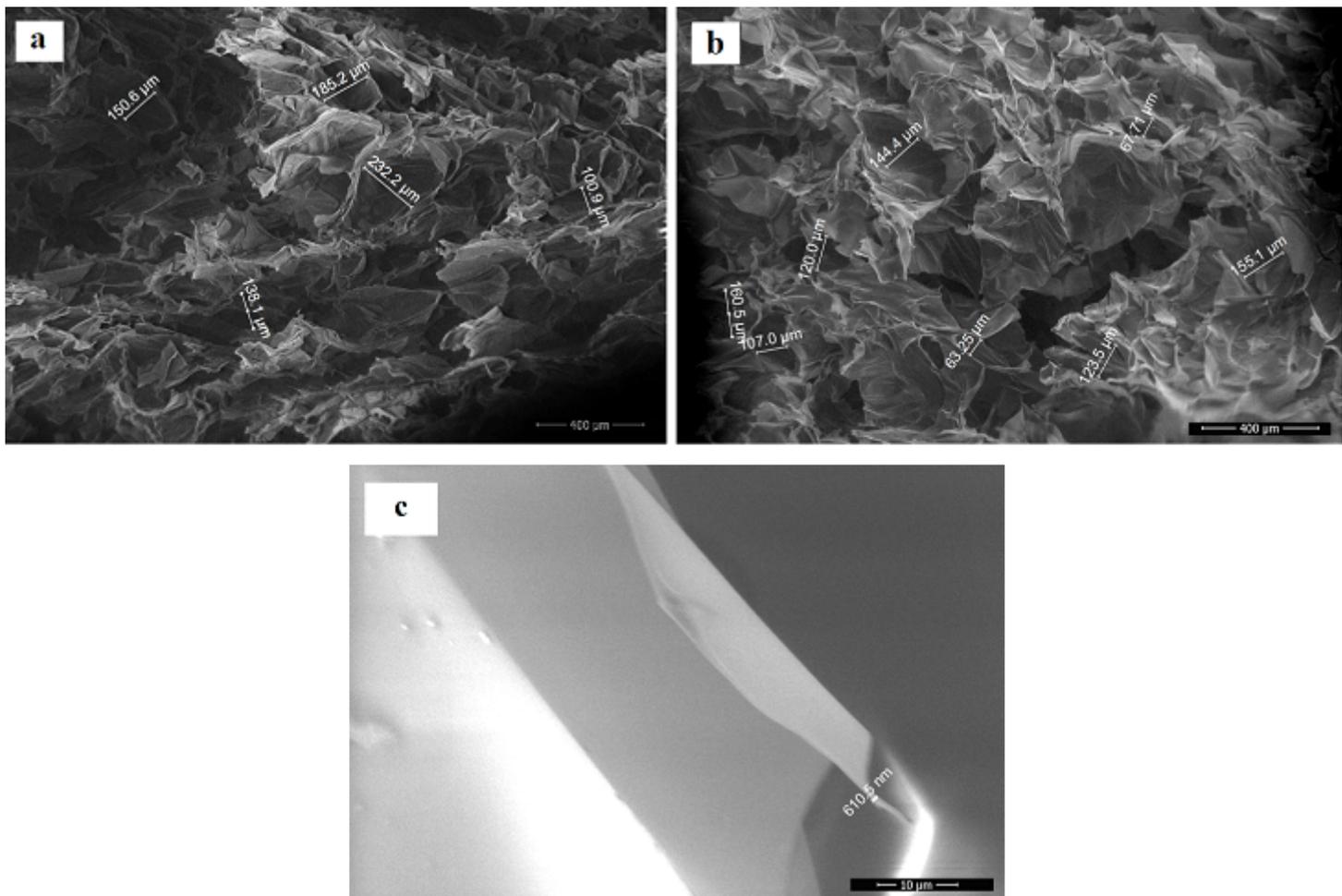


Figure 4

SEM images of fractures of the initial chitosan aerogel (a) and chitosan aerogel modified with a 3-wt.% solution of poly(GMA-co-HeMA) copolymer (b) at 165× magnification, with a 3-wt.% solution of poly(GMA-co-LMA) copolymer (c) at 2500× magnification

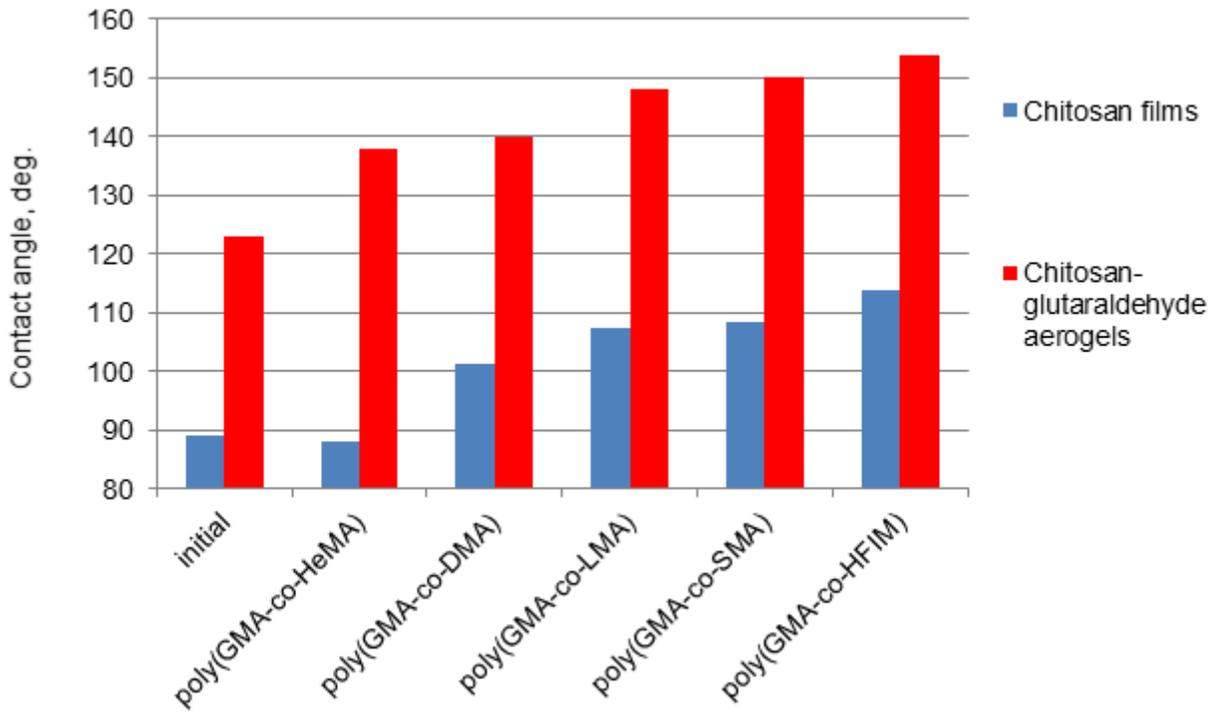


Figure 5

Effect of the structure of the hydrocarbon substituent of GMA- and AIMA/FMA-based copolymers on the contact angles of the resulting materials (blue - chitosan films; red - chitosan-glutaraldehyde aerogels)

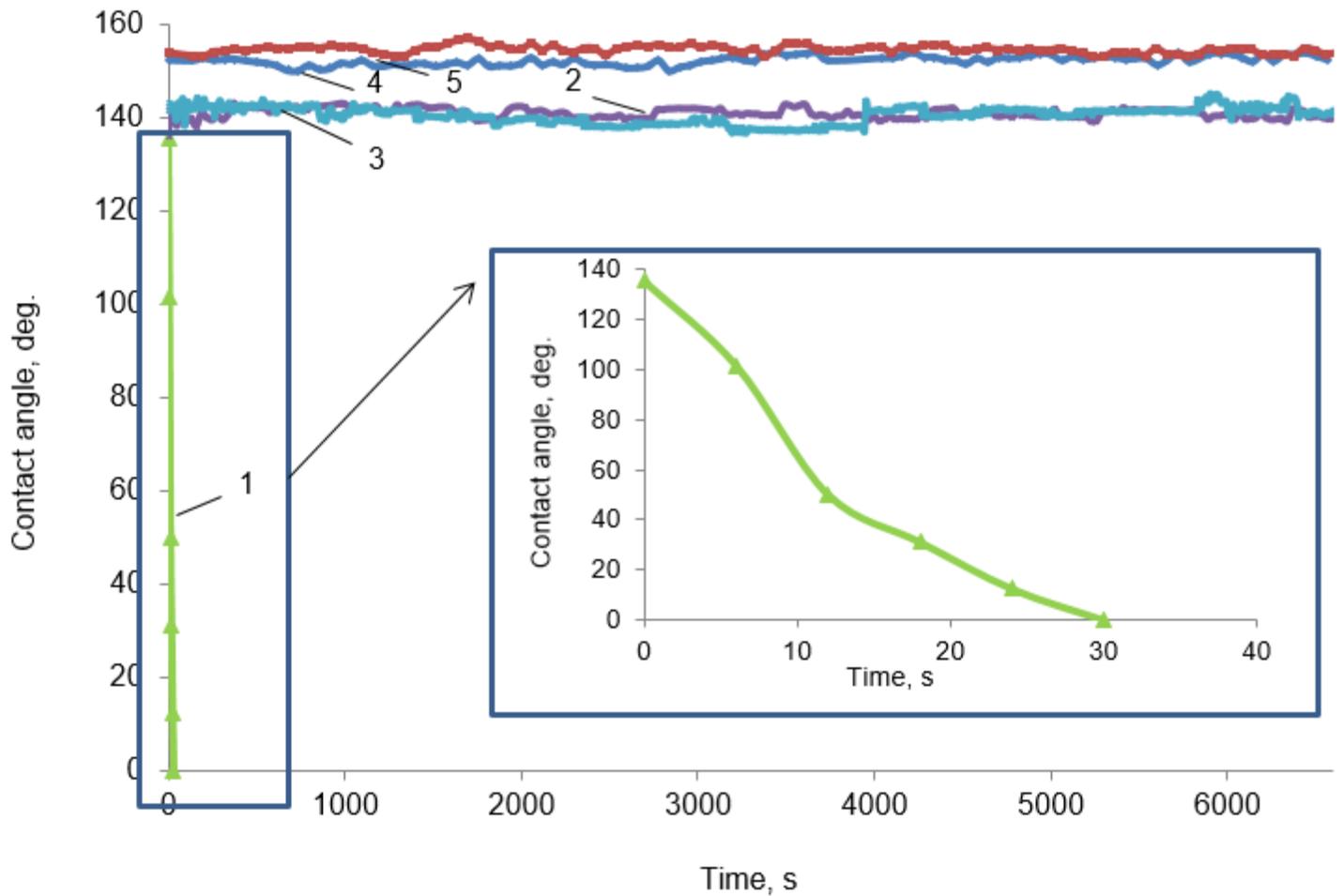


Figure 6

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

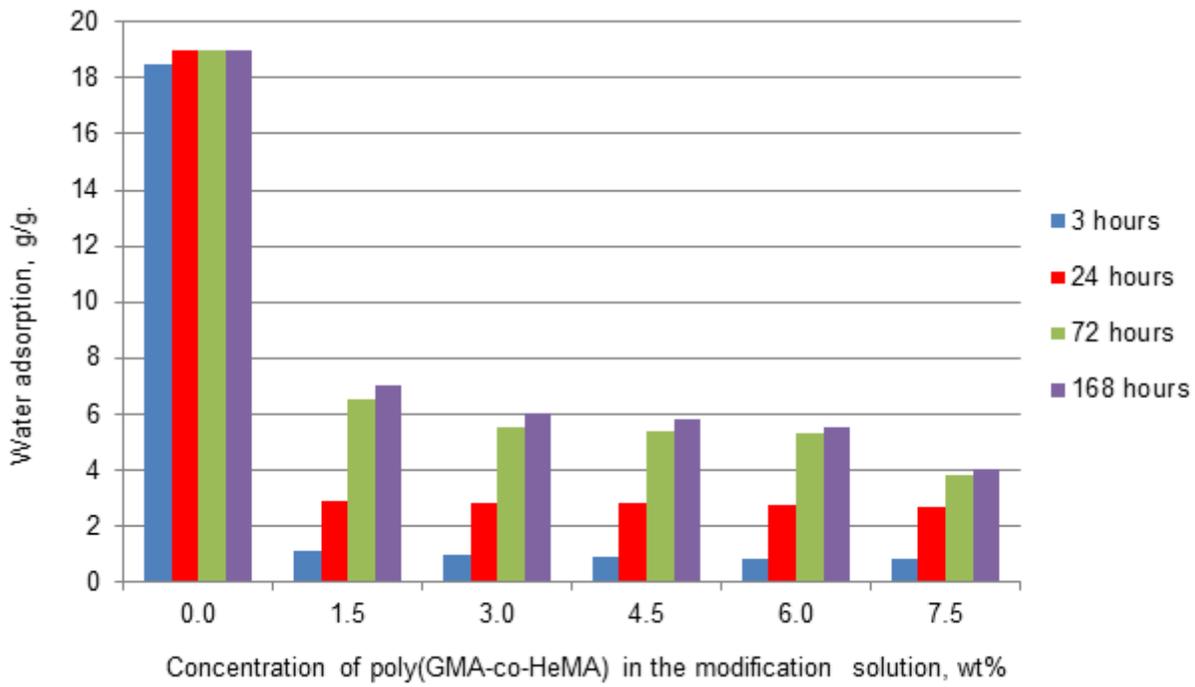


Figure 7

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

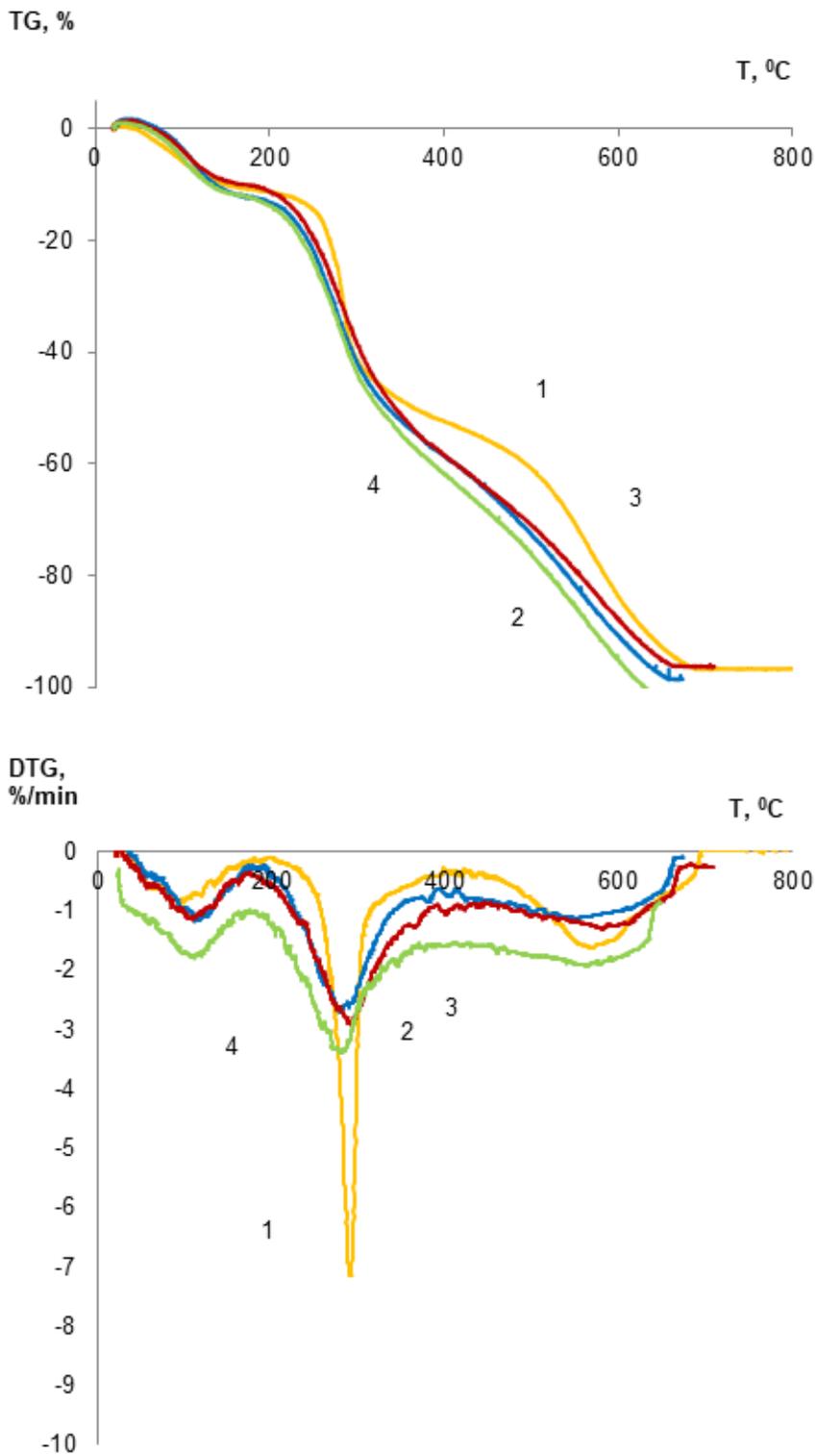


Figure 8

Weight loss curves (TG) and differential thermogravimetry curves (DTG) for the unmodified chitosan film (1) and aerogel (2); aerogels modified with poly(GMA-co-HeMA) (3) and poly(GMA-co-LMA) (4)

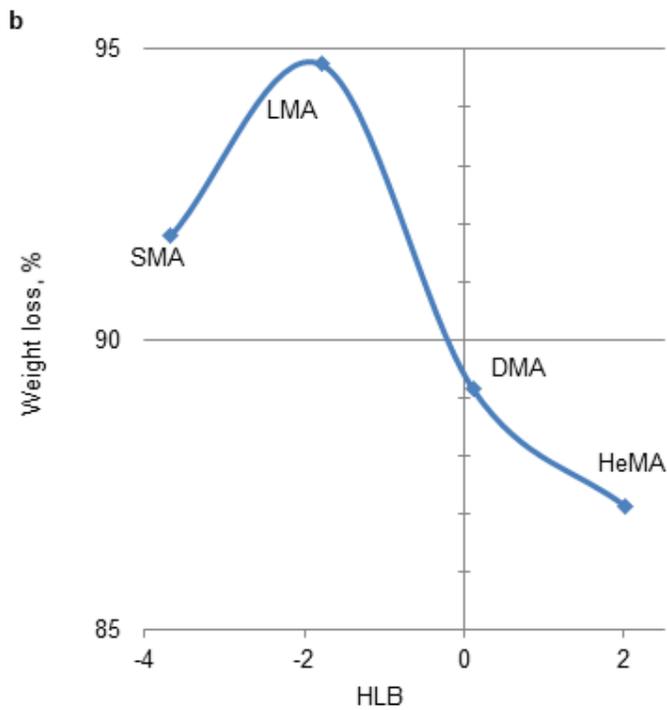
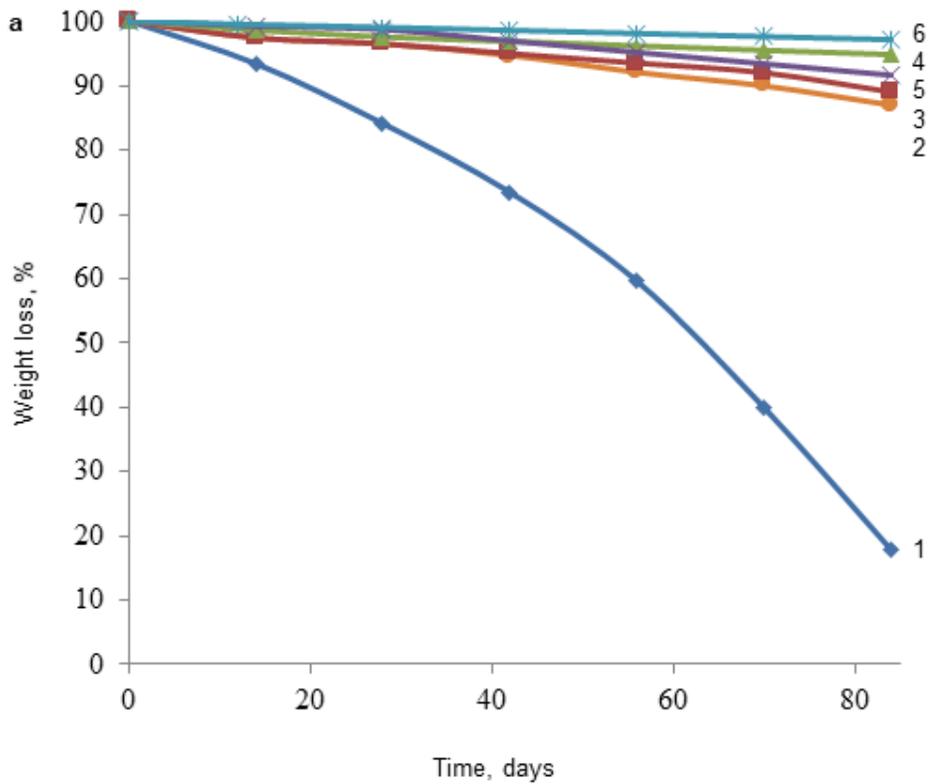


Figure 9

a) Biodegradability of the initial (1) and modified (2 - poly(GMA-co-HeMA); 3 - poly(GMA-co-DMA); 4 - poly(GMA-co-LMA); 5 - poly(GMA-co-SMA); 6 - poly(GMA-co-HFIM) chitosan films from the weight loss of samples versus time and b) comparison of weight loss after 84 days for samples modified with GMA- and AIMA-based copolymers with HLB data