Synthesis of polymer ion-exchange hydrogels under γ - irradiation ^{60}Co

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Abstract. We have reported earlier about the modification of ion-exchange hydrogel under the influence of gamma radiation. The optimal absorbed dose of irradiation had been choosen for radiation modification of polymer hydrogels by ionits to produce products with a high content of the gel - fractions and sufficient mechanical properties. The dependence of the static exchange capacity of hydrogels on the type of ionit and its fractional composition had been studied. The dependence of the static exchange capacity of the quantitative composition of the ionit in the volume of the hydrogel had been investigated. The ion-exchange medical eye lenses had been made under selected conditions of synthesis. Their sorption properties had been studied.

1. Introduction

Nowadays polymeric medical supplies are widely used in many areas of medicine. Therefore polymeric materials with desired properties are especial interest when it contacts with a human, for example, hydrogels. Their creation is possible by synthesis of new or modification of known materials. The basic requirement for hydrogels is their biological inertness, which is primarily depends on the conversion degree of the monomers. One of the ways to hydrogels preparation is radiation polymerization. Polymerization of various monomers, high conversion of monomers, high purity polymers synthesized, ease of process control, are advantage of the radiation technology [1], [2], [3], [4]. Various modifications of hydrogels for soft contact lenses (SCLs) with specified properties can be synthesized by this technology.

SCLs are effective treatment of fresh chemical and thermo-chemical eye burns by neutralize the damaging agent, the acceleration of the cornea epithelialization, preventing of the simblefarona, and at a later date – after of burn corneal healing.

SCLs show the best sorption capacity than saline solutions, it is not large enough. The increasing of SCLs sorption capacity to searing chemicals, toxins, viruses and bacteria, results in the increasing of their therapeutic activity in the treatment of burns and viral eye lesions.

The goal of this paper is to study the synthesis of polymeric ion-exchange materials in the form of the soft contact lenses for the treatment of chemical and thermal burns, trauma and infectious diseases of the eye, by the radiation modification of hydrogel by ion-exchange resins. The hydrogel for SCLs had been used to prepare an ion-exchange polymer hydrogel [5].

2. Material and methods

The samples were irradiated with ^{60}Co γ-rays at 310 K. The dose rate was measured with a Fricke dosimeter, assuming the radiation yield of Fe to be equal to 15.6 (100 eV). The dose absorbed by the sample was calculated using the mass energy absorption coefficients.

The hydrogel has been prepared by radiation copolymerization of methyl methacrylate and N-vinylpyrrolidone in the presence of divinyl ether diethyleneglycol under γ-irradiation [6]. It has a high (70%) water content, plasticity and stability. Lenses from this hydrogel are used for vision correction (from -30D to +30 D), and as therapeutic lenses in diseases such as bullous keratopathy, keratitis, corneal transplants, and others.

Weakly acid cation resins (KB-2E - methacrylic acid-divinyl ether diethyleneglycol (DVEDEG), KB-4 - methyl ester copolymer of methacrylic acid, divinylbenzene (DVB), and D-113 (Granion CWP-1) - copolymer "acrylic" and DVB) were used as modifying agents for polymeric ion-exchange hydrogel synthesis [7]. Modifiers with fraction 0.25-0.35 mm and less than 0.25 mm have been investigated.

The content of the gel-fraction can be calculated as

$$X=(m_2/m_1)\times 100, \%, \quad (1)$$

where m1 is weight of the sample before the extraction; m2 is weight of the sample after the extraction. The average value of six measurement was used.

The deformation and strength characteristics of the samples were studied by tensile machine RMB 30. Strength at failure (puncture) σ is

$$\sigma=k\sigma\times(P/(h\times d)), \text{ kgs/cm 2 (MPa)}, \quad (2)$$

where P is load at which the sample was destroyed, kgs; h is thickness, cm; d is diameter of the sample working area, cm (0.4 cm); kσ is normalization factor (1.1).

Deformability ε is calculated as

$$\varepsilon=k\varepsilon\times(l/d)\times 100,\%, \quad (3)$$

where l is elongation, the value of the indenter sliding from the beginning of its contact with the sample to sample destruction, mm; kε is normalization factor (2.2).

The determination of cross-linked polymer (gel-fraction) in modified ion-exchange resins and in the original hydrogel samples was performed by extraction with distilled water during 36 hours in Soxhlet apparatus. After extraction the samples were dried in a vacuum oven at 60 ° C to constant weight.

The acid-base titration has been used for estimated of sorption activity.

The absorption of alkali from 0.02 M of solution NaOH, for samples of hydrogels modified by ion exchangers in the H-form, has been determined. The absorption of the acid from 0.02 M of HCl solution for hydrogels containing ionits in Na-form has been determined. The hydrogels were placed in the successive volume of 0.02 mmol/g acid or alkali solution and it was titrated to determine static exchange capacity (SEC) of acid or alkali.

3. Results

Figure 1 displays the results of the cross-linked polymer determination in the ion-exchange hydrogel samples prepared at different absorbed doses. As seen, the increase of absorbed dose results in increase the degree of monomers. Lower content of gel-fraction in the modified by ion-exchange material vs the hydrogel may be due to the breakage of the polymer chain on the modifier, which does not react. The gel-fraction content is closed to 100% at absorbed doses high than 25 kGy, e.g. 35-40 kGy.

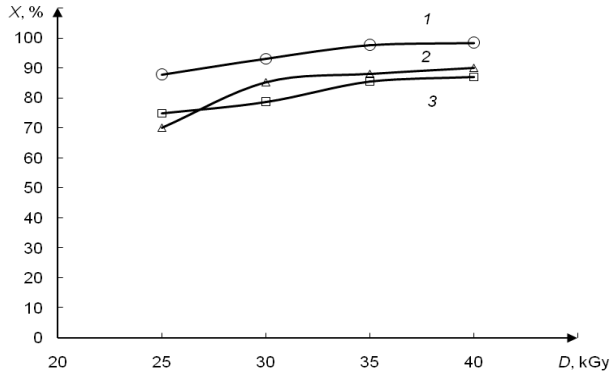

Figure 1. The content of the ion-exchange polymer hydrogels gel-fraction vs absorbed doses of irradiation. 1 - hydrogel; 2 - hydrogel +5% D-113; 3 – hydrogel +5% KB-4.

Figure 2 displays the results of the strength and elongation at puncture tests for ion-exchange hydrogel samples containing 5% resin D-113, irradiated with different doses. As seen, the tensile strength at puncture values are below at the higher deformability values for samples irradiated with dose 35 kGy. The strength values of the material increase with increase of the absorbed dose but it loses elasticity. So, the value of absorbed dose is equal to 33-35 kGy has been choosing for synthesis of ion-exchange hydrogel samples.

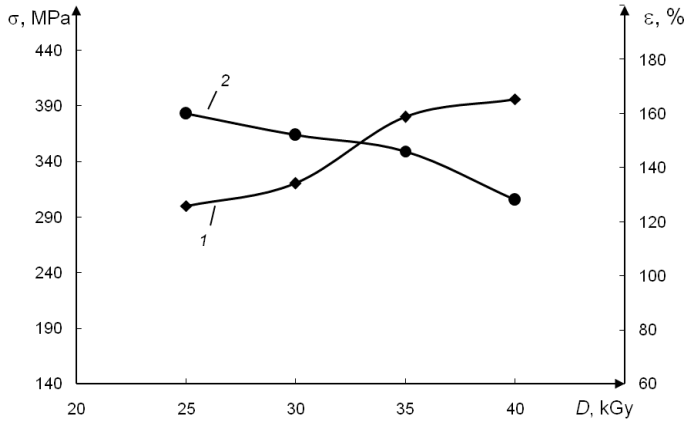

Figure 2. The strength characteristics of polymer ion-exchange material vs absorbed doses of irradiation. 1-tensile strength puncture (σ); 2-deformability (ε).

In previous studies the content of modifiers in ion-exchange samples was 5%. The SEC is not high enough for such content. Therefor it was studied SEC for higher modifiers content. Figures 3-4 displays the dependence of SEC of acid and alkali by ion-exchange hydrogels with different fraction from saturation time. As seen, the SEC to acids and alkali of the fractional composition of ion-exchange resins with fraction 0.25 <d <0.35 mm are higher than for the fine fraction. SEC of hydrogel modified by ionit D-113, is up to ~1.2 and 3-fold to the acid and to the alkali 2-2.5-fold, than SEC materials modified by ionits KB-4 and KB-2E, respectively. So, the cation exchanger D-113 has been choosing for subsequent studies.

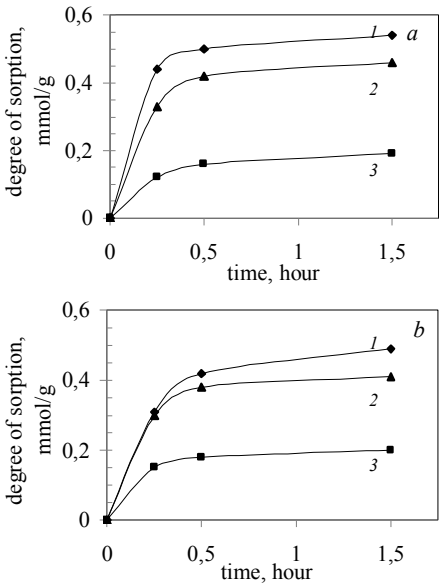

Figure 3. Absorption curves of HCl by ion-exchange hydrogels. Modifiers (5%): 1 - D-113, 2 - KB-4, 3 - KB-2E. Fraction of modifier: a) 0.25 <d <0.35 mm, b) d <0.25 mm.

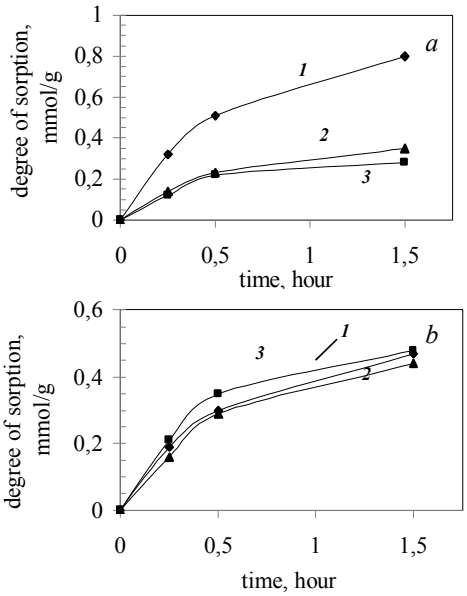

Figure 4. Absorption curves NaOH by ion-exchange hydrogels. Modifiers (5%): 1 - D-113, 2 - KB-4, 3 - KB-2E. Fraction modifier: a) 0.25 <d <0,35 mm, b) d <0.25 mm

Figure 5 displays the dependence of the SEC hydrogels containing 5, 10, 15% of the ion-exchange resin to alkali from saturation time. The dependence of the SEC from saturation time to acid is the same. As seen, the increase of the ion-exchange resin content in the hydrogel has been resulted in a significant increase of the sorption capacity.

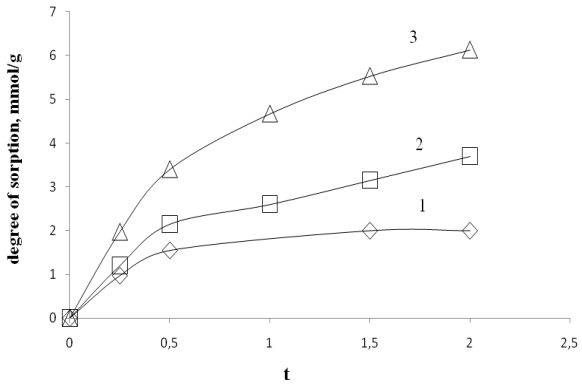

Figure 5. Dependence SEC of the IEMEL containing 5, 10, 15% of the ion-exchange resin to alkali from saturation time.

Ion-exchange medical eye lenses (IEMELs) were prepared by absorbed dose 35 kGy, the contain of cation exchanger D-113 (fraction 0.25 <d <0.35 mm) is 15 %.

Figure 6 displays the dependence of the SEC of ion-exchange medical eye lenses and hydrogel lens to alkali and acid from saturation time. As seen, the first lenses SEC value to alkali is equal to 6.2 mmol/g for two hours. IEMEL SEC to acid is increased rapidly (30 min) and then it becomes constant and equal to ~3mmol/g.

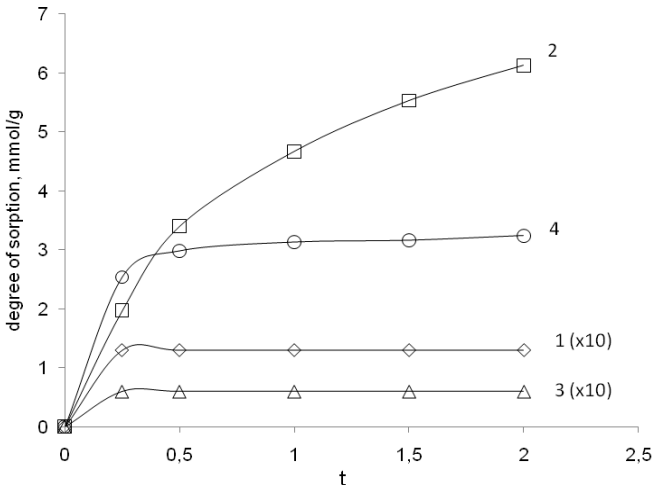

Figure 6. Dependence SEC of the IEMELs (15% of modifiers) from saturation time. SEC of alkali: 1-lens of hydrogel, 2-IEMELs; SEC of acid: 3-lens of hydrogel, 4- IEMELs.

4. Discussion

Biocompatibility is basic requirement for medical devices in contact with the human body. Biological inertness of polymer material provides a high degree of conversion of monomers, under which is not possible to disengage into the human body incomplete polymerization products. The study of depending on the content of gel fraction on the absorbed irradiation dose was performed 25kGy dose at which the monomer mixture is polymerized to the solid state. Increase of the dose to 35kGy allowed to extend the content of the gel fraction to 90%. Further increase of the absorbed dose had no significant effect on the change of the degree of conversion of the monomers.

The absorbed dose of irradiation also affects the processes of cross-linking and destruction of the polymer, which leads to change of the strength characteristics of the hydrogel. Study of the strength characteristics showed in the range of 25 to 40 kGy of the absorbed dose, that at higher absorbed doses of irradiation the breaking strength of the hydrogels had been increased, but at the same time their elasticity had been decreased. As seen from Figure 2, the strength and the deformability of the hydrogel have optimal values at the absorbed dose 33 kGy. The absorbed dose γ-irradiation 35kGy had been selected during the comparison of the results obtained for the synthesis of polymeric ion-exchange hydrogel.

SEC investigation of the dependence of ion-exchange polymer hydrogels on the type of cation resins and its fractional composition (Fig. 3 - 4) showed that as a modifier the ion-exchange resin D-113 fraction from 0.25 to 0.35 mm is preferable to the use. A smaller fraction of cation resins beds and stick together during polymerization, which leads to reduction of its active sorbent surface.

However, absorption of acids and alkalis in the ion-exchange hydrogel is determined not only by the properties of the sorbent, and the processes of diffusion of sorbate in the hydrogel matrix. The nature of the polymer and its moisture content affects on sorption and desorption of substances. In hydrogel materials diffusion rate of solutes generally increases with increasing water content. Simply increasing of the percentage of the sorbent in the hydrogel will reduce the moisture content and, consequently, to reduce the rate of diffusion of adsorbed substances. Changing the composition of the polymerization mixture in the direction of increasing the hydrophilic component and reduce the amount of crosslinking agent, helped to keep the water content, increase the amount of ionit to 15% and get ion exchange hydrogels with high adsorption activity (Fig. 5). A further increase of ion exchangers is possible provided that the basic properties of the base of the hydrogel.

Studies of the sorption properties of ion-exchange medical of eye lenses (Fig. 6) showed that IEMEL actively absorbs alkali for 2 hours or more, and the sorption of acid is almost complete within 30 minutes. The lens swells and gradually increases in size at the sorption of alkali. This is due to the

fact that, in parallel with the sorption of alkali ion exchanger s in the hydrogel matrix flow processes of alkaline hydrolysis of polymethyl methacrylate to form polymethacrylic acid. Spatial grid is loosening the hydrogel water content and increase the absorption of alkali. Not appropriate to use for the sorption of alkali IEMEL more than 2 hours since the size of the lens is increased significantly distorted her boarding radius and this lens will not be comfortable to the eye. During the sorption of acid IEMEL lens gradually shrinks and diffusion of sorbate in its scope is difficult. Thus, efficient use of time to retrieve IEMEL acid is 30 minutes.

5. Conclusion

The samples of ion-exchange materials had been obtained in the result of conducted studies by the radiation modification of polymer hydrogel soft contact lenses.

The absorbed dose at which had been achieved the highest possible value of the content gel - fraction and strength characteristics selected.

The cation resins D-113 with fraction 0.25 <d <0.35 mm showed the best results of sorption activity in the studied range of ion exchangers.

The quantitative content of the ion exchange resin was increased to 15% for increase the sorption capacity of ion-exchange polymer hydrogels, subject to changes of the ratio of monomers and cross-linking agent in the base hydrogel.

The eye treatment ion exchange lenses made in the chosen conditions of synthesis. Sorption activity EMIEL exceed the value of static exchange capacity of contact lenses on the acid 50-fold and 47-fold on the alkali.

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