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Key Words

Macromolecules; Materials; Polymers; Nanoparticles; Metal

Mini Review

Radiation-Chemical Methods of Hydrogel Dressing Structure Modification

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Abstract

The objects of the study are polymeric composites synthesized by mixing chemically and structurally complementary natural (Agar-Agar [AA], Chitosan [CS]) and Synthetic (Poly-N-Vinylpyrrolidone [PVP]) macromolecules in the presence of low molecular weight substrates (Polyethylene Glycol [PEG-400], Glycerol [GL]) as plasticizer to regulate the surface properties and volume characteristics of hydro-gel materials with functionally specified operational parameters, such as high adhesive affinity to damaged tissues, biological compatibility with body and organ fluids, high esterase and antimicrobial activity.

Introduction

Hydrogel composites based on complementary natural and synthetic polymers are soft and porous materials, their structural and molecular hierarchy and functionality are close to biological tissues. New products are developed for biotechnology, tissue engineering, medicine and cosmetology in the form of various composite materials of wide application range, in particular, systems with controlled drug re-lease, wound or burn-preventive dressings. The hydrogels produced by chemical cross-linking or physical "freezing" are not stable and require fixation of the structure using additional, often toxic cross-linking reagents [1-3]. Radiation-chemical modification is an environmentally friendly and technological method for producing high-purity composite hydrogels, as well as a very effective way to increase their strength, wear resistance and biocompatibility with simultaneous sterilization of the final product. The use of high-energy radiation energy is referred to the category of "green" technologies, since it reduces to a minimum or excludes highly toxic chemical reagents as crosslinking agents from precursors in preparation of three-dimensional matrices of polymer compositions of highly toxic chemical rea-gents as cross-linking agents and is characterized by the absence of low-molecular-weight toxic products of polycondensation reaction and recombination of short-lived active radicals, such as ammonia, hydrogen sulfide, etc.

Results and Discussion

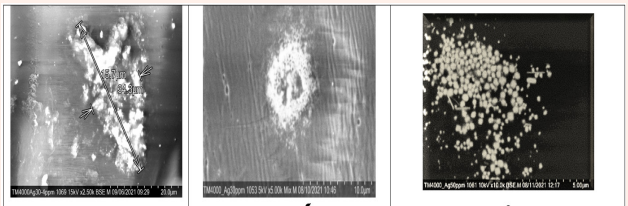
In our previous study [4], we considered the mechanism for formation of rare cross-linked composite hydrogels based on the natural polysaccharide Agar-Agar [AA], a synthetic polymer for medical application, Poly-N-Vinylpyrrolidone (PVP), synthesized by electron irradiation method. It has been established that synthesis conditions and component composition of the initial mixture determine the structure and morphology of the formed composite hydrogel and their mechanical properties. A new interpretation of the formation of the composite hydrogels structure in the presence of various plasticizers was provided. It was shown that formation of a three-dimensional structure of PVP occurs as a result of electron irradiation of the reaction mixture in an aqueous medium in the presence of low- and high-molecular plasticizers, the content of which can be controlled to obtain networks of various strengths and elasticity. Composite hydrogels P[AA]:[PVP]:[plasticizer] represent a model of interpenetrating networks, consisting of physical and covalent cross-linking sites, which give them a good com-bination of elastic and strength properties. One of the most perspective polymers for creation of wound hydrogel dressings is the biocompatible and biodegradable Chitosan (CS), resulted from partial deacetylation of chitin. Chitosan, in addition to gel-forming and film-forming properties, also exhibits antimicrobial properties due to the blocking of the anionic phosphate groups of bacterial phospholipids in the cell membrane by amino groups, which prevents their reproduction [5-7].

This article describes the study of the radiation-chemical method for production of hydrogel dressings based on a composite mixture of Polyvinylpyrrolidone (PVP): Chitosan (CT): Agar-Agar (AA) in Lactic Acid (LA) medium with the addition of Glycerol (GL) at various ratios of the components. The most optimal ratio of components that satisfies the required mechanical parameters for the use of polymer hydrogels as antibacterial dressings, in which they exhibit high adhesive affinity to the dermis, elasticity and mechanical strength, corresponds to the composition [AA]:[PVP]:[PEG]:[CS] = [0.5÷1.0]:[7÷10]:[1.0÷1.5]:[0.25÷0.5] wt. % respectively. The FT-IR spectra of the initial materials and their radiation cross-linked forms show that the main matrix of composite can be represented as a combination of physical interweaving of agar and PVP with surface modification of the macromolecular chains of the latter with PEG-400 oligomers [4]. The main contribution to the formation of covalent crosslinking sites is made by the synthetic polymer, while the natural polysaccharide can be considered as a "matrix-proform" where the process of destructive crosslinking of PVP takes place. This conclusion was made according to the fact that the FT-IR spectra did not reveal the formation of a new or disappearance of the initial functional groups of polymers, except for the shifts of the characteristic absorption bands of functional groups of polymer chains due to changes in the electronic environment and the variations of their intensities as a result of the crosslinking effect. The process of three-dimensional polymer hydrogels formation based on chitosan, that belongs to the category of polymers with an amorphous-crystalline structure, occurs similarly.

The advantage of chitosan is the presence in its macromolecule of hydroxyl (-OH) and primary amino groups ($-NH_2$), which carry a positive charge in aqueous media at acidic and neutral pH values, which determines the possibility of forming a polysaccharide in a nanostructured state. For example, in [6] based on chitosan and its derivatives, NPs with sizes from 20 nm to 100 nm were obtained by ionotropic gelation and precipitation coacervation. The yield of NPs (in terms of freeze-dried) was 83.0% depending on the quantitative ratio and concentration of the components used, as well as the influence of various external influences. There is a growing interest in the production of Metal Nanoparticles (MNP) in polymer compositions. The silver nano-particles are most demanded for application in biology and biomedicine, both for therapeutic

purposes and to visualize the severity of various diseases due to their high therapeutic activity, inertness, biocompatibility and lack of toxicity [8]. The hydrogen peroxide in the concentration range from 0.3 to 0.5 wt.% was used in order to obtain chitosan with an optimal degree of polymerization and to improve its characteristics, that allowed to increase its solubility in water. Irradiation of chitosan in the presence of PVP and agar provides more elastic properties with a high degree of composite moisture. Silver ions were introduced into the volume of the prepared composite in the amount of 10, 30, and 50 ppm prior to irradiation with an electron beam at the pulse linear accelerators of electrons ILU-10. From the analysis of spectral data of hydrogel composites with silver ions it can be assumed that carbonyl groups of pyrrolidone ring of PVP and the primary amino groups of glucosamine cycle of chitosan are the centers of silver ions concentration due to the formation of coordination bonds with un-shared electron pairs of electronegative heterogenic atoms in polymeric matrices. Besides, when compo-site hydrogel is irradiated in the presence of silver ions, an electron-stimulated process of the formation of colloidal particles of silver ions ensembles takes place according to the Mott-Henry theory: during the photochemical or electron reduction the hydrated electron migrates and gets captured in the coordination "trap" at the interface or near the diffusion layer surface of silver ions resulting in the formation of nanoparticles or clusters of silver ions both bound and free from coordination with the functional groups of polymers [8,9].

Thus, the formation of silver nanoparticles in the volume of the composite hydrogel can be considered as an electron-stimulated process of their reduction to the atomic state as a result of the capture of a hydrated electron by the coordination sphere of metal ions. The electron microscopic studies of composite hydrogel samples based on chitosan with silver ions were carried out to confirm these assumptions (Figure 1). It has been established that the formation of silver nanoparticles in the volume of a hydrogel can proceed in two different modes. According to the first mode the reduction of silver ions up to atomic state occurs before the process of the composite hydrogel irradiation with photons of UV radiation. In the second mode the reduction of silver ions occurs during the process of radiation exposure. It was shown that in the first case of preliminary irradiation of a silver-containing hydrogel composition in the UV region, large aggregates of irregularly shaped silver ion ensembles are formed, while in the second case, aggregates accumulate in a certain area of a spherical shape (Figures 1a & 1b, respectively). With the growth of silver ions concentration from 10 ppm to 50 ppm, a simultaneous reduction of silver ions is observed, both coordinated with electron-donating atoms of the functional groups of macromolecules of the hydrogel composition and free silver ions (Figure 1c).



а	б	с
Ag 30ppm	Ag 30ppm	Ag 50ppm
UV-radiation	e-radiation	Mixed radiation (UV and e-beams)

Figure 1: SEM data of silver ion metalized composite hydrogel obtained in different modes.

The following scheme can be presented for formation of silver ion metallized composite hydrogel:

$$R-\underset{(PVP)}{N-C=O}\cdots\cdots\left(Ag^{+}\right)_{n}\cdots\cdots\underset{(CS)}{NH_2-R}\xrightarrow{e_{hydrat}}R-\underset{(PVP)}{N-C=O}\cdots\cdots\left(Ag^{0}\right)_{n}\cdots\cdots\underset{(CS)}{NH_2-R}$$

It is noticeable that a considerable strengthening of the mechanical properties of composite materials is observed with the growth of silver ions content in the hydrogel (Figure 2).

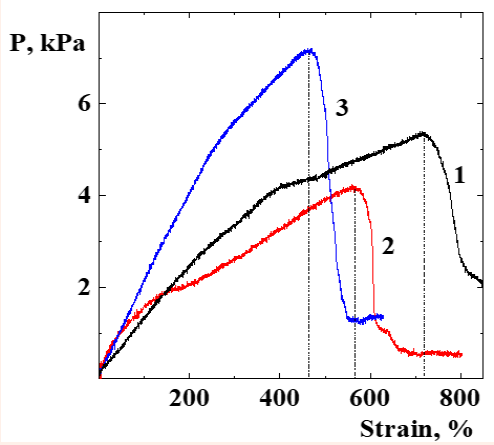


Figure 2: Change in shear stress of composite hydrogels on stretching. P[PVP]:[AA]:PEG] (1); P[PVP]:[AA]:PEG]:Ag (10 ppm); P[PVP]:[AA]:PEG]:Ag (30 ppm)

The obtained data allow to predict a possible molecular mechanism of self-assembled systems formation and are of great applied importance. It can be assumed that the including of $-NH_2$ and N-C=O functional groups into the hydrogel composition can be used for self-assembly of silver nanoparticles into supramolecular aggregates in an aqueous medium. This is of great practical importance since their physical-chemical and physical-mechanical properties as well as their biological activity and toxicity significantly depend on the size, shape and poly-dispersity of NPs [8-10]. Experiments on probing the adhesion of synthesized polymeric hydrogel dressings to a solid substrate (a metal cylindrical rod 10 mm in diameter) showed that the compositions are characterized by a mixed type of destruction fracture, which allows them to be classified as ideal adhesive materials. The thermogravimetric studies (Figure 3) testify in favor of sorption of an excess amount of water molecules strongly associated with the functional groups of macromolecules of the network. It has been established that with the growth of dressings hydrophilicity due to the stepwise hydrophilization by the stage-by-stage introduction of lyophilic components into the volume of hydrogel, there is a shift in the extreme point of desorption of bounded water towards its increase in hydrogel composites in the series: P[PVP]:[PEG]=7.0:1.5 wt.% (107 °C)<[AA]:[PVP]:[PEG]=1.0:7.0:1.5 (111°C)<P [AA]:[PVP]:[PEG]:[CS]= 1.0:7.0:1.0:0.25 (115 °C).

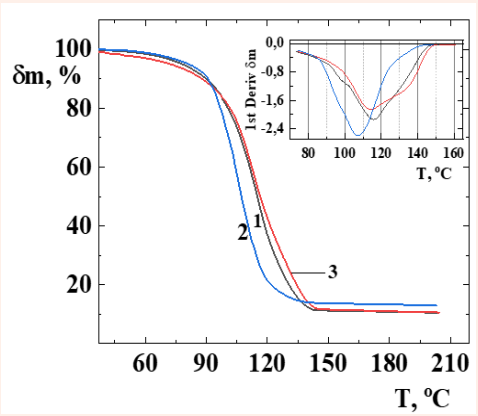


Figure 3: TGA data of P[PVP]:PEG]=7:1 (1); P[AA]:[PVP]:[PEG]=1.0:7.0:1.5 (2); P[PVP]:[AA]:PEG]:[CS]=1.0:7.0:1.0:0.25 (3) wt %.

Thus, the presence of reactive functional groups in the chitosan macromolecule and its solubility in aqueous solutions provides the possibility of various chemical modifications of the polysaccharide according to the reactions of polymer-analogous transformations, by graft and block polymerization.

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