

Mechanical Properties and Characterization Mineral Filled Hydrogel Wound Dressing

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Abstract

The mechanism of formation of slightly crosslinked composite hydrogels based on natural agar-agar polysaccharide, synthetic polymers for medical purposes - Poly-N-Vinylpyrrolidone (PVP) and low-molecular plasticizers (polyethylene glycol PEG-400 and glycerin) in the presence of mineral fillers (bentonite, montmorillonite and shungite) synthesized by electron irradiation was considered from the point of view of analyzing their mechanical characteristics under various types of applied efforts. It is established that the synthesis conditions and the component composition of the initial mixture determine the formed structure of the hydrogel composites and their mechanical properties. A new interpretation of the formation of the structure of composite hydrogels in the presence of various plasticizers and mineral fillers is given. A detailed analysis of the deformation curves of composite hydrogels is presented taking into account the visco-elastic, highly elastic and forced-elastic states.

Keywords: Composite polymer hydrogels; Electron irradiation; Plasticizer; Deformation; Compression; Stretching; Elasticity

Introduction

Hybrid micro- and nanocomposites represent a promising class of complex polymer-inorganic materials in which mineral particles are distributed in a polymer matrix of synthetic or natural origin [1-3]. The study of structure and properties of minerals of the layered aluminosilicates class and carbon matrix, produced from available and widespread natural raw materials, is an important scientific and practical task aimed to create new multifunctional materials. The specific structure and composition of natural minerals, artificial and synthetic polymers makes it possible to obtain a new class of functionalized composite materials with unique properties, which are applied successfully in different sectors. This is mainly defined by uniqueness of the physical-chemical properties of layered aluminosilicates and shungite, which appear in a developed specific surface, the presence of active reaction centers, high adsorption and ion exchange abilities. This suggests the possibility of using bentonite clays and shungite in medicine as drug carriers in the form of gel, film and injectable drug forms and wound dressing. The main conditions for the use of polymer-mineral composite materials for medical purposes are uniformity of the natural mineral composition, harmlessness of the components and relative indifference of their behavior in the polymer matrix.

This article reviews the mechanism for formation of intercalated structures of a natural mineral particles in the volume of a polymer matrix, synthesized by the method of electron irradiation of solutions of natural (AA) and synthetic (PVP) polymers mixtures in the presence of plasticizers. The choice of the electron irradiation method is connected to the fact that it is the most optimal and acceptable method for obtaining three-dimensional polymer structures with the required mechanical properties to use in medical practice due to the destruction of PVP macromolecules with forming crosslinked matrix. Other options for cross-linking of a linear PVP are possible only by means of thermal degradation at the temperature of decomposition of the material at a temperature above 120 °C in a dry state, which is not acceptable for our purposes. Moreover, the electron irradiation is a pure reagent-free method

for obtaining three-dimensional polymer systems, which solves the issue of sterilization of polymer compositions, which is the main condition for their application in medical practice for use as an anti-burn and an anti-bedsores hydrogel coated on damaged tissue.

Experimental

Preparation of a composite hydrogel solution included two stages: 1) dissolution of the required weight of PVP at a temperature of 15 °C with stirring on a magnetic stirrer until complete dissolution, after which plasticizer PEG-400 (P1) was added to this solution. Separately, a solution of agar-agar (P2) was prepared in distilled water at a temperature of 80-90 °C for 2 hours. Next, solutions P1 and P2 were mixed with addition of 0.5g (0.5%) of dry bentonite, montmorillonite or shungite powder with vigorous stirring until a homogeneous system with a uniform distribution of the mineral component (for 1-2 hours) was obtained until a suitable temperature (40-45 °C) is reached for pouring the polymer-mineral mixture into the special shaped containers. Irradiation of a mixture of prepared solutions of polymer-Inorganic Compositions (PIC) of a given composition was performed in an accelerator ILU-10 with electron beam in the dose range from 5 to 25kGy in special plastic molds with a rectangular cross section of 10x12cm cm or in cylindrical ampoules with an inner diameter of 10mm and a height of 30mm. The samples, obtained at the irradiation dose of 25kGy, were used in the work.

Description

In our previous study [4], we considered the mechanism of formation of rare cross-linked composite hydrogels based on the natural polysaccharide agar-agar and a synthetic polymer poly-N-vinylpyrrolidone, synthesized by electron irradiation. It has been established that the synthesis conditions and component composition of the initial mixture determine the structure and morphology of the formed hydrogel composites and their mechanical properties. A new interpretation of the formation of the composite hydrogels structure in the presence of various plasticizers was provided. The morphology of the polymer film is represented by macro porous segments with a developed surface and topological inhomogeneity typical of amorphous sparsely crosslinked polymer systems. It is characterized by a layered structure or cleavage of layers caused by formation of a matrix of an Interpenetrating Network (IPN) with alternating layers of natural (agar-agar) and Synthetic Polymers (PVP) with lateral grafting of plasticizer molecules (PEG or glycerol). When forming a hybrid composition of mineral-IPN aluminosilicate particles are unevenly distributed over the interlayer surfaces of the interpenetrating network. Particularly noteworthy is the shape of mineral particles, which resemble the structure of γ -alumina. Traditionally, its crystal structure is described as feldspar, in which aluminum atoms are localized simultaneously in tetrahedral and octahedral positions, as a result of which its surface is much more hydroxylated compared to silica gel. It has been noted that the presence of water accelerates the rate of aluminum hydrolysis with formation of a lamellar large-pore structure of aluminum hydroxide, which also has an octahedral structure.

However, in the system studied by us, the particle sizes determined according to SEM data go far beyond nanoscale, in particular, the average size along the diagonal of octahedrons varies from 3.04 to 5.57 μm , that is, it exceeds the interplanar distances between layers by three orders of magnitude. Therefore, the alternative explanation can be provided, according to which, in addition to delamination or exfoliation of bentonite particles in the intertwined polymer matrix of the interpenetrating PVP-AA network, micro crystallites of mineral particles grow into more or less large aggregates in the form of a single monolithic structure of the same geometry as for individual molecules of hydrated alumina in the form of well-formed octahedra. Thus, exfoliation begins with the splitting of sheets along the boundary of the gallery $\text{Si-O-Al-O-Si} \equiv [\text{mMe}^{n+} \text{ kH}_2\text{O}] \text{Si-O-Al-O-Si} \equiv$ with subsequent destruction of the three-layer structure along the heterobond line Si-O-Al along the oxygen atom. When mineral particles are in a polymer matrix consisting of two complementary and intertwined macromolecules associated with the terminal hydroxyl groups of plasticizers, the exfoliation process can proceed until the complete rejection of not only sheets of aluminum phyllosilicates from each other, but also by splitting the structures of polyoxosilicon and polyoxoaluminum chains into separate fragments in the form of disparate $\gamma\text{-Al}_2\text{O}_3$ octahedra.

An increase in the interlayer space during exfoliation of silicates by the IPN matrix contributes to the further process of delamination of the layered filler due to growth of disjoining pressure between the packages and, subsequently, between the sheets of the packages. It is logical that irradiation of the system with an electron beam aggravates this process, since exposure to various types of radiation leads to formation of radiation defects, in which there is an uncontrolled redistribution of crosslink sites, and the dimensions of the pore structures of the polymer matrix, in which more or less hydrated particles of bentonite are initially located according to the law of average statistical distribution with non-linear effects during structural transitions. It can be assumed that during electron irradiation of the $\text{P}[\text{AA-PVP-PEG}]\{\text{Mineral}\}$, after partial exfoliation of mineral filler sheets from each other by polymer macromolecules, the stage of aggregation of disordered aluminosilicate sheets with each other begins already along the side faces and edges of aluminum octahedron oxide, forming associates with more or less individual molecules of alumina or silicon oxide or from their linear sequences. Consequently, recrystallization of bentonite nanoparticles into larger perfect crystals, consisting mainly of aluminum oxide, takes place. The absence of silica tetrahedral structures can be associated with a higher rate of its hydrolysis and dissolution in a water-alcohol medium with formation of polysilicic acid or their associated forms with a polymer matrix through hydrogen bonds according to the scheme compared to aluminum oxide.

Complete destruction of clay packets in the form of separate plates leads to formation of a layered structure, which is well distributed in the polymer matrix. It should be noted that under real conditions, complete exfoliation of all layers of the clay mineral is a difficult task. This structure, in comparison with the intercalated

structure, provides the most favorable improvement in the characteristics of the resulting polymer nanocomposites due to the high aspect ratio and intense surface reaction of clay particles with polymer chains. The strength properties and deformation behavior of mineral filled hydrogel compositions are clearly illustrated by the stress-strain dependence ($P=f(\epsilon)$), obtained by the method for determining the "puncture" strength of a material by pressing a ball through a layer of a flat composite hydrogel. Three main sections can be distinguished on the deformation curves. The initial, gently sloping rectilinear section corresponds to the area of plastic, the second - to elastic, the third - to viscous-flowing deformation. In the interval of sections II-III, phase transitions and orientation of macromolecular chains take place between crosslinking sites in the direction of the applied tension and compression force, at which the segment mobility of macromolecules increases, and the structure of the material is rearranged.

In section III, the relaxation rate of the material becomes comparable with the strain rate of the sample. Outside the zone III, with further deformation, macrocracks appear in the sample of mineral filled hydrogel composition, as a result, the thinning section of the composite hydrogel, which bears the load from the indented ball, is punctured from region I to region III. It is important to have a qualitative representation of the process leading to strengthening or weakening of the strength of the composite material under external loads to establish quantitative relationships between the structure and the property of a material to resist destruction. It is now generally known that absorption of the energy transferred to the polymer matrix occurs almost entirely. The function of mineral fillers is to promote and control deformations in the matrix, providing significant stress concentrations in those places where local deformations can be initiated. Shear fluidity plays a role in the process, but crazing is the predominant hardening mechanism. Many researchers have shown that stress whitening is associated with formation of more crazes than microcracks [5]. With regard to the system we are considering, it can be assumed that mineral fillers play the role of stress absorbers caused by compression or tension of the sample.

The stress-strain dependence does not show a region of elastic deformation corresponding to the Hooke model. The dependence $P-f(\epsilon)$ already at the initial stages resembles a plastic deformation profile, that is, not a sharp, but a gentle change in shear or compression stress up to ϵ 20%, which is not typical for most previously studied systems [6]. When a sample is compressed in the region of ϵ 30-50% there is a "Consistent" orientation of mineral particles and layers of polymeric planes of a three-dimensional matrix, along the axis of tension or compression. It is natural in this case to expect some change in the morphological structure of the hybrid composition, which corresponds to the bend section on the stress-strain curve during compression, which is not observed in the absence of a mineral filler [7]. Any parameter that affects the degree of intercalation and delamination, like the modulus, has a significant effect on the tensile strength of nanocomposites. Another effect of the mineral filler on the mechanical characteristics

of hydrogel composites is the value of elongation at break, which is affected by the interfacial reaction between the polymer and layered silicates and shungite. In addition, introduction of a mineral filler into the volume of the polymer matrix resulted in a decrease in the degree of elongation by almost a factor of two. In shear zones [6], molecules are oriented approximately parallel to the applied tensile stress and, therefore, normal to the planes where crazes form. Since both the initiation and growth of crazes are inhibited due to orientation in this direction, shear bands have an effect on inhibition of the crazes growth. As the number of shear bands increases, the length of newly formed crazes decreases. We propose to consider such hybrid composite materials as a new class of interpenetrating networks with promising applied properties (materials for tissue engineering and anti-burn hydrogel dressings with a wound healing effect and high bactericidal activity, etc.).

Conclusion

Thus a systematic study of the synthesis of hybrid composite materials based on synthetic (PVP) and natural (AA) macromolecules in the presence of plasticizers (PEG-400, glycerol) and the mineral filler (bentonite, montmorillonite and shungite) was carried out. The XRD analysis and SEM showed that the structure of resulting hybrid composites is defined as an interpenetrating network, in the volume of which intercalated particles of the mineral component are distributed. It has been established that the mechanical properties of the hybrid composition are determined mainly by structural organization of the interpenetrating polymer network formed during electron irradiation of the initial polymer mixture in the presence of plasticizers, as well as by the conditions for intercalation of polymer segments into the interpacket layers of the mineral matrix. During the process of crazing of the sample under tension the shear stress is concentrated in the central part of the sample from the periphery of the fastening. It is shown that the degree of swelling of the hybrid composition strongly depends on concentration of a low molecular plasticizer in the polymeric interpenetrating network, which can easily impregnate into the interplanar layers of mineral matrix.

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