

Study of Composite Carrier Based on Organic and Inorganic Polymers

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Summary: In this work, the possibility of obtaining composites on the basis of polyvinyl alcohol and bentonite clay Manrak deposit has been investigated. The interaction of polyvinyl alcohol with bentonite clay was studied by employing methods such as equilibrium swelling, sedimentation, electrophoresis, viscometer, and scanning electron microscopy. It was established that the interaction of polyvinyl alcohol and bentonite clay are due to the hydrogen bonding between them. The composite gels with the improved structural-mechanical and prolonged effect have been formed on a base both of polyvinyl alcohol and clay.

Keywords: Composition, Polyvinyl alcohol, Bentonite clay, Hydrogen bonding

Introduction

The significant role of polymers, particularly gels in reducing toxicity, increasing the duration (prolongation) of release as well as and controlling release of medical substances is widely known and well documented [1, 2]. Development of the polymer composites with improved structural and mechanical properties has an immense significance. In medicine, they can be used as a support for the active constituents [3].

To achieve these objectives, along with chemically cross-linked polymer gels, physical gels are also important, which are capable of self structuring. Medicinal substances can be introduced into the structure of the physical gel during their formation, thus avoiding time-consuming and laborious stage of washing of the unreacted monomers, initiators and other harmful impurities [4, 5].

However, as low mechanical and thermal durability is peculiar to organic physical gels so low ability to self-structurization and absence of the elastic properties worsening quality of the medicinal form are characteristic for bentonitic clay. At the same time, the lack of polymeric carriers used in this direction, makes researchers to search for new carriers [6-8]. To be a useful drug carrier, a polymer needs to possess certain features. The polymeric composite carrier has to be non-toxic, non-immunogenic and biocompatible. The carrier must contain an effective dose of active agent; the material of system must biodegradable or form biologically acceptable degradation products. The carrier must be able to be easily sterilized. A number of natural

polymers like polysaccharides and synthetic polymers like segmented polyurethanes has been successfully used as polymeric drug carriers [9, 10].

In this work, we have investigated the possibility of preparation of new composite carriers of drug substances based on inorganic (bentonite clay) and organic polymer (polyvinyl alcohol (PVA)). Our aim was to obtain composite carriers with improved properties based on their components.

Results and Discussion

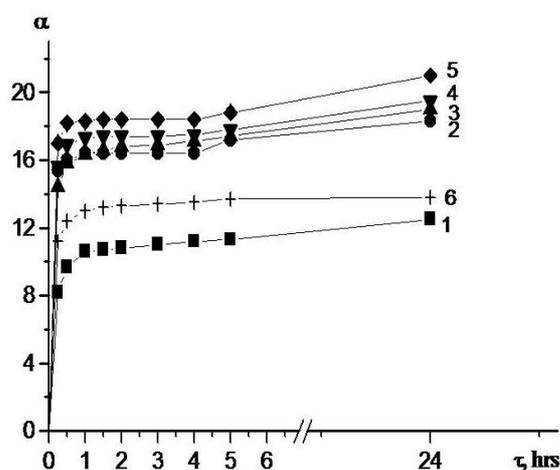
To achieve the optimal composition, conditions of obtaining and controlling the properties of composite materials are essential to be understood, including laws of interaction between their components.

In this connection the nature of interactions of the given polymer-clay systems was investigated by employing methods such as equilibrium swelling, the sediment analysis, rotational viscometer, scanning electronic microscopy, and electrophoresis.

According to the kinetics of swelling of bentonite clay in water and solutions of PVA, some increase in the degree of swelling of clay in the polymer solution was observed, as compared to water (Fig. 1). However, at higher concentration of polymer, such as >0,5%, a decrease of swelling was observed. In this system, the interaction may be based on hydrogen bonding. At low concentrations of the polymer due to single contact of PVA with particles of clay, a complex is formed, probably due

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to hydrophilization of disperse system, and an increase in degree of swelling is observed. At the same time, it is known that interaction of disperse systems with linear polymers results, in flocculation. The flocculation mechanism is based on certain concentrations of polymer in system. This corresponds to the concentration dependent degree of swelling, namely the area of concentration higher than 0.5 %. In this area, flocculated clay particles form dense flocs, which lead to a decreased of swelling. To explain such behaviour of clay in polymer solution, it is necessary to take into account the nature of bentonite clay and PVA, and also to consider the possible mechanism of their interaction. It is known that the clay surface has a negative charge due to the hydroxyl groups. PVA is non-ionic polymer having the secondary hydroxyl groups.



1 - Water; [PVA] = 2 - 0.01 %; 3 - 0.05 %; 4 - 0.1 %; 5 - 0.5 %; 6 - 1 %.

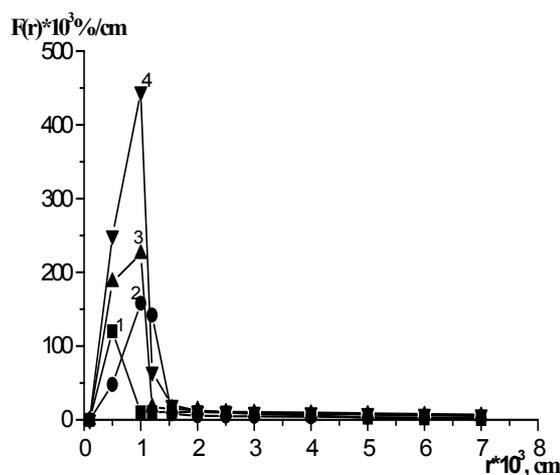
Fig. 1: Kinetics of swelling of clay in water and PVA solutions.

It is therefore safe to assume that the interaction between PVA and clay are due to the hydrogen bonding. At low concentrations of polymer, increasing the hydrophilic character of the dispersed system is possible due to single collisions of clay and PVA particles. In the field of high PVA concentrations, the flocculation forces start to function. As a result, the flocs are formed and clay swelling is reduced.

In physiological solution of PVA, the degree of clay swelling was almost twice less than in aqueous solutions. It can be explained on the basis of

action of high ionic forces in NaCl solution. On the other hand, these results further confirm the polyelectrolytical properties of nonionic polymer PVA, due to bentonitic clay.

The results of sedimentation analysis shows that clay basically consists of particles of size 10^{-5} M, both in water and in PVA solution (Fig. 2). Insignificant integration of clay particles in polymer solutions (not more than 10^{-5} M), and also preservation of stability of clay compositions are important for pharmaceutical application.



1 - Water; [PVA] = 2 - 0.01 %; 3 - 0.05 %; 4 - 0.5 %.

Fig. 2: Differential curves of clay sedimentation in PVA solutions.

FTIR Spectra of PVA-clay compositions indicated the formation of a polymer-clay complex due to intermolecular hydrogen bonding. In IR spectrum of a PVA-clay composition, absorption bands due to a H-bonded polyassociates appeared in the range of $3400-3000\text{ cm}^{-1}$; intensive strips of H-bonds of chelate type and CH_2 -, CH -groups PVA at $2939, 2914\text{ cm}^{-1}$; deformation stretching of crystallization waters of clay, and flat deformation stretching of OH-groups at $1714, 1663, 1441\text{ cm}^{-1}$; asymmetric stretching of Si-O-bonds and deformation stretching of C-OH-bonds at $1332, 1239, 1143, 1094\text{ cm}^{-1}$; deformation stretching of OH-groups at $916, 848\text{ cm}^{-1}$; deformation stretching of Si-O at $606, 479\text{ cm}^{-1}$; Besides this, new absorption bands appear at 2034 cm^{-1} , probably due to formation of new organic-inorganic bonds, such as C-O-...Si or C-O-...Al (Fig. 3).

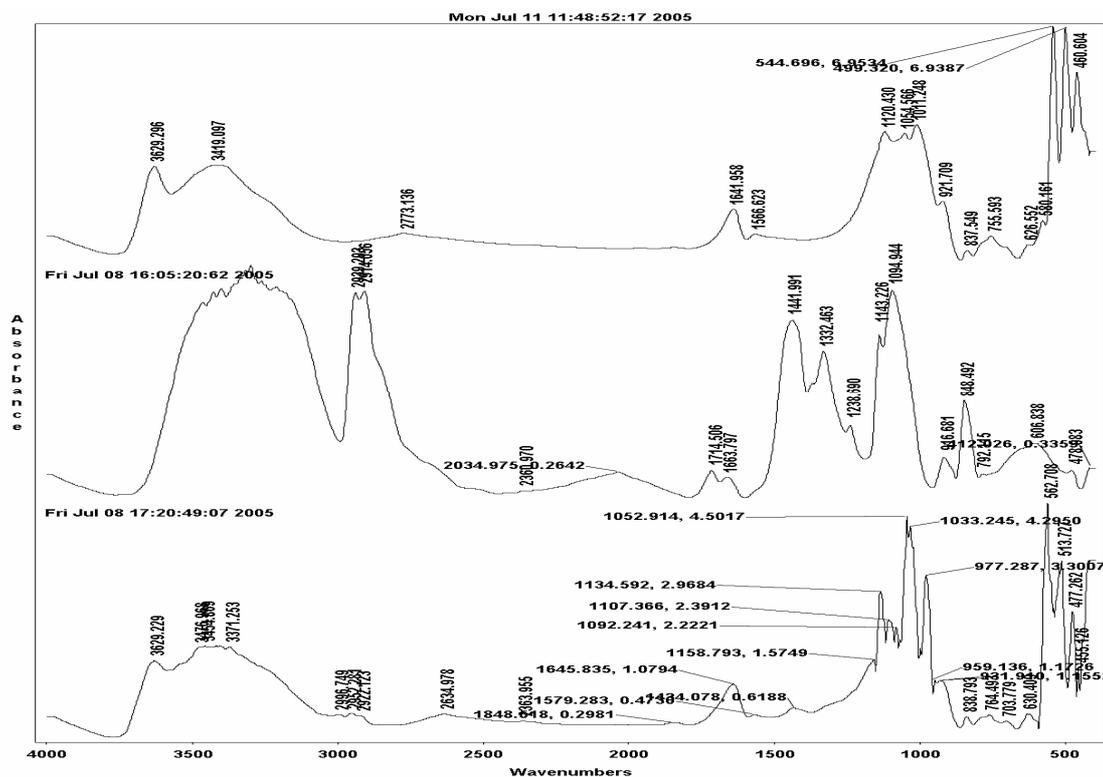


Fig. 3: IR-spectra of clay (1); PVA (2); and PVA-clay composite (3).

Electrokinetic studies further confirm the mechanism of interaction, as presented in the Table-1. The scanning electronic microscopic studies were carried out to investigate the morphological structure of composite complexes PVA-clay. The results of studies are presented in Fig. 4 (a, b, c). From the presented data it is possible to infer that complexes of bentonite clay - PVA consist of homogeneous microstructural units with the size of ~1-3 μm. As for literature data, due to interaction of polymeric chains in physical gels, such microstructures as aggregates, micelles, multiplets and crystallites are formed. The size of these microstructures is within 1 - 100 nanometers. On the basis of this, it is possible to infer that the composition PVA-clay consists of crystallites of initial polymers. The size of particles depends on clay particles composition. It is necessary to note that the formation of the complex leads to ordering of the structure of composition.

Table-1: Values of electrokinetic potential of bentonite clay and its compositions with PVA. [Clay]=0.25 %.

n=[PVA]/[BC]	0	0.01	0.02	0.04	0.016	0.018	0.02	0.04
ζ, V	-0,18	-0,1	-0,11	-0,12	-0,14	-0,16	-0,15	-0,14

We also studied the ability of gelation of solutions of PVA, bentonite clay and their compositions by using rotational-viscosimetry.

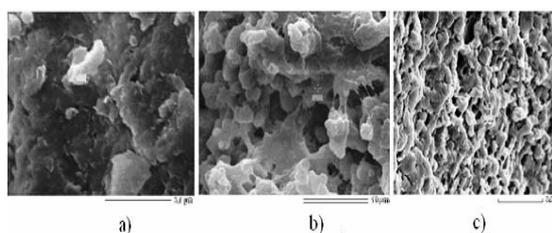
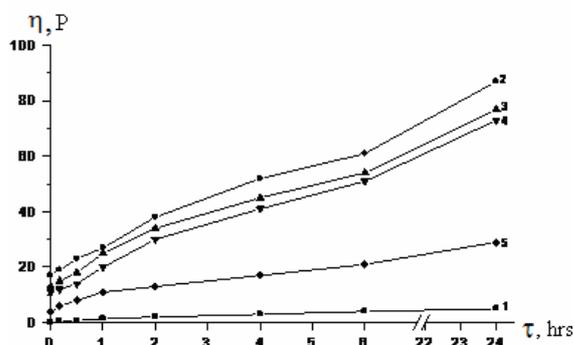


Fig. 4: SEM images of (a) BC; (b) PVA (c) BC-PVA composition.

The results of rotational-viscometric studies (Fig. 5) indicated that the viscosity of PVA-BC compositions is between the pure gel PVA and bentonite clay. Formation of composite gel was achieved fully in a twenty-four hours, and the value of plastic viscosity comes to the value of limit does not change any further. Gel-forming ability of composition gels with maintenance of PVA 75 and 50% is between the clay and PVA. The increase in the content of clay composition results in decrease of viscosity and increase in content of PVA. This ability

of structuring of composite gel is basically because of the PVA.



(1) – BC; (2) – PVA; [PVA-BC] - (3)-75:25; (4) - 50:50; (5) - 25:75.

Fig. 5: Kinetics of structure formation of gels bentonite clay-PVA.

Compatibility of PVA and bentonite clay is observed by viscometry and visually. Homogeneity of composition is related to the formation of water soluble complex with components interacting with each other. The complex of bentonite-PVA is probably stabilized due to hydrogen bonding. Bentonite-PVA composite were also examined as interpenetrative nets. Interaction of components due to unCoulomb forces makes them compatible with each other. In case of the formation of electrostatic complexes, solubility of product would decrease due to decrease of homogeneity.

In our previous work, we have studied sorption and desorption of alchidine from composite gel [11]. The study of kinetic curves for sorption of alchidine components, such as polysaccharides (PS), proanthocyanidins (PA) and amino acids (AA) over composite gels showed that the equilibrium is achieved between 2-3 hours. For further studies, the data were recorded for 3 hours. The study of desorption of alchidine components from the composite gels indicated its prolonged effect. From those studies, we can conclude that the composite gels have the capacity to be used for the medicinal preparations.

In this work, we studied the morphological structure of composite gel, containing alchidine. The data of electronic microscopy of BC-PVA compositions with alchidine is presented in Fig. 6. Due to hydrogen bonding, the basic components of alchidine-proanthocyanidins and polysaccharides form a complex with composite materials. Being high-molecular superficially active substances, these

compounds disperse the composite particles even stronger and form interpolymeric complexes. As a result, the system is formed which is homogeneous in sizes and less dispersive, in comparison with the particles of a composition.

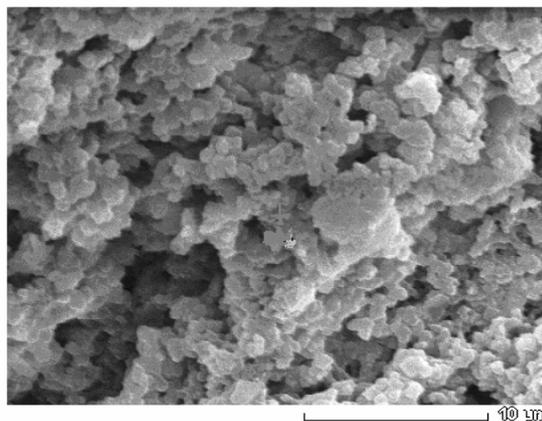


Fig. 6: SEM images of BC-PVA-alchidine composite.

Experimental

In the present study, the bentonite clay (BC) of the Manrak deposit (East Kazakhstan) was used. Purification of bentonite clay was carried out by employing the method of D.P. Salo [12]. Polyvinyl alcohol (PVA) ($[-CH_2-CHOH-]_n$, $M=80000$, type 16/1) was used without additional purification.

The degree of gel swelling was determined by the equilibrium swelling method and counted against the volume of swollen sample to the volume of dry sample [13]. Sedimentation analysis of bentonite clay was carried out by the method of Figurovsky [14]. Electrophoresis mobility of polymer blends was measured in a slightly modified instrument of Rabinovich and Fodiman with moving boundary [15].

FTIR Spectroscopy

For all synthesized polymer-clay gels, as well as for initial substances, IR spectra were recorded by using spectrophotometer "Satellite" FTIR firm "Mattson" (USA) with Fourier transformation.

Scanning Electron Microscopy (SEM)

The morphology and structure of composite gels were studied by using a scanning electron

microscope JEOL JSV-638F with EDS-detector (Japan). The samples were placed into tubes and gold-coated in Quick Auto Coater and then studied at 15-20 kV.

Rheological Experiment

The rheological properties of the composite gels were studied by using the rotation viscosimetry (Brookfield DV-II+PRO (USA)).

Preparation of Composite Polymer

The composite gels on a base of natural polymers were prepared, as shown in the Fig. 7. Briefly the calculated amount of polymer was blended with water and mixed thoroughly, until homogeneous mass (343-353 K) was obtained. To this homogenous mass, the calculated amount of bentonite clay was added. The resultant gel was cooled to room temperature and kept in refrigerator at 0° C till further use.

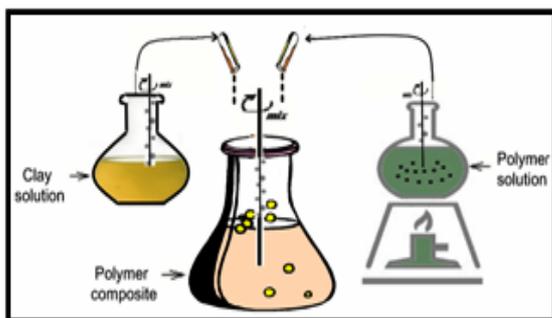


Fig. 7: Schematic drawing of the preparation of polymer composite.

Conclusion

By using methods of equilibrium swelling, sedimentation and electrophoreses, the mechanism and kinetic of interaction between bentonite clay and PVA has been studied. These composite materials meet the medical requirements of stability, compatibility and uniformity. It was demonstrated that the colloidal-dispersive composites are stabilized by hydrogen bonds and flocculation forces. That's why the formation of composite complexes was found to occur due to the hydrogen bonding. Equilibrium sorption of alchidine components is reached during 3 hours. The order of sorption was observed for components: proanthocyanidins and polysaccharides. Study of desorption of alchidine indicated its prolonged effect. Studies show that these

composite gels have the prospective to be used as the supports for the medical compounds.

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