Nanopolymeric blends on the base of polysaccharides and their derivatives for biocapsulation

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Introduction

In this report the results of investigations are presented connected to creation of ecologically safe, biodegradable biologically - active water - soluble nanopolymeric systems for agriculture, medicine, pharmacy and biotechnology.

It is known that water-soluble polymeric systems find the wide use in various industry branches, medicine, pharmacy and agriculture as solutions, films, granules, carriers of biologically active substances etc. Their use is connected with the possibility of utilization without discharge of toxic products of destruction, ecological safety, technologisity etc. The great role of water soluble polymers is assigned to decision of agroindustrial complex tasks.

Analysis of polymer use in agricultural production allows to allocate 2 directions of polymeric systems creation, possessing the biological activity. It is the development of polymeric multicomponent matrices on the base of water-soluble polymers and synthesis of polymers with own activity. Moreover, for widening of these polymers action spectra by modification it is possible to include into polymeric system various by their activity type components-fungicides, bactericides, insectoacaricydes, plant growth and development regulators.

At present the special attention is paid to the investigations, connected to creation of nanopolymeric materials of various use, which find the most application in medicine, pharmacy, biotechnology and the other spheres of human activity.
As the nanoparticles (NP), a particles are implied where at last one of dimentions has to be no more than 10-100 nm. From there position high crystalline polymers (cellulose, chitin, polyamides, silk fibroin) are considered as monostructures where crystallites play specific role of NP.

Polymeric NP can be effective matrices for immobilization of various drug substances and their transport through biological membranes whereas in some cases they possess own biological activity (especially NP of native polymers and their derivatives). It seems very effective to use polymeric NP for biological macromolecular. DNA, macrofags etc incapsulation. For the same purpose (incapsulation) polymeric NP may fond use in agriculture and nanobiotechnology.
Actuality of this work consists in creation of nanopolymeric systems on the base of native polysaccharides and their derivatives to use in agriculture as ecologically save, biodegraded, high effective polymeric forms of plant protection chemical means or matrices - carriers for various physiologically active substances.

Material and methods

The work main purpose - creation of water-soluble polymer-polymeric mixtures on the base of polysaccharide derivatives, obtained from local raw materials (methylcellulose, Na-

carboxymethylcellulose, chitosan, pectin) and some synthetic polymers (polyvinylpirrolidone, polyvinylcaprolactam, polyvinylalcohol etc.) of different composition, investigation of their compatibility on molecular and supermolecular levels, structure and properties with the aim to use them as a polymeric systems possessing by own biological activity or a carriers for physiologically active substances.

Earlier, we proposed water-soluble polymeric systems coverings, possessing by setted complex of physico chemical properties and high biological activity for capsulation of cotton, cereals, vegetables, and other agricultures. The technology consist of seeds surface treatment by water-soluble polymeric covers.

The principles of objects choice is based not only on the availability of local raw material resources (wastes of silk production - silk worm chrysalises, cotton-refining plant wastes - linter, wastes of juice production - pectins), but also on the possibility to create on their base the systems with own biological activity. The possibility to couple two polymers of different molecular structure and nature in different or similar phase state, by varying of solvent nature opens the wide possibilities for formation of nanopolymeric materials with the use of various methods for their synthesis.

We choose the next main methods of NP, NS obtaining:
1. Film casting from polymers solution in weak acetic solutions and their mixtures of various concentration (0,1%, 0,5%, 1-2%) and different components ratio for NP and NS formation in the process of solvent evaporation and transition solution-solid phase.
2. Choice of precipitators which mix with water (acetone, methanol etc) up to suspension formation followed by NP formation control in TEM.
3. The same as 2, combined with ultrasound treatment (US) for various time.
4. Creation of micro- and miniemulsions of inverse type (oil-water) with intensive US irradiation following solution Ph change to convert polymers in the insoluble form.
5. Creation of so called template in the form of form with "pitted" nanostructures.
6. As we have above noted to reach the necessary properties of polymeric systems we choose very productive method of polymer-polymeric mixtures creation on the base of native and synthetic polymers. When use of such way of modification we discovered the formation of nanoparticles and nanostructures. We mean the formation of the special structures which have nanometric dimensions.

At present we are developing the scientific bases of nanoparticles (NP) and nanostructures (NS) formation in two-component mixtures of native and synthetic polymers. It's clear that in this process in the case of polymers with the tendency to self-organization the optimal variants of mixing are two native polymers or one native and the other synthetic. At formation of NP and NS in this system the determined factors are: components ratio, solution concentration, molecular mass, solvent nature, components compatibility, chains stiffness, internal influence etc.

The optimal range of solution concentration -0,1-0,5%. NP forming polymer is preferable to create NP in the mixtures. Strong macromolecules salvation does not favour to NP formation as well as high molecular masses, especially in the mixtures because can't provide high packing density which is necessary the nanoproperties to be displayed. At the same time very short chains have strong stiffness, that interferes their dence packing.
Polymers phase state doesn't influence significantly on NP formation because in the polymer mixtures, crystallization processes are suppressed. So, the phase state is as self- regulating because joined structure-formation isn't observed in polymers (pectin for example where the NP formation is very complicated). Thus in the plane of NP obtaining the optimal are low or middle

degree of crystallinity (30-50%).The exception are high crystalline native polymers (cellulose, chitin) which have NP with very high crystallinity, caused by specific features of biosynthetic process and that provides very high packing dencity which is so necessary for nanoproperties to be shown.

We are developing the effective method of homogeneous polymeric NP (in the base of separate polymer) and heterogeneous (from polymers mixture synthesis with the use of improved method of microemulsions of oil-water and water-oil type. The discrete nanoparticles and matrices with included polymeric NP have been obtained. The examples of such systems are chitosan - PVA, CMC - PVA, PC - PVA, CMC - chitosan, chitosan - acrylic acid copolymers. In these systems, dependiny on concentration hybride NP including both polymers or film- like matrices with NP inclusion are formed. It has been shown that acrylic acid substitution on its copolymers under mixing with chitosan led to formation larger NP that evidently caused by more complex structure of second component.

Results and discussion

With the goal to establish the influence of various factors on the structural, thermodynamical, physico-chemical and physico-mechanical properties, the systems obtained were investigated by complex of physical and physico-chemical methods, namely scanning and transmission electron microscopy, optical microscopy, X-ray diffraction, IR-spectroscopy, determination of thermodynamically (Δgx-average energy of free mixing) and physico-mechanical parameters and their biological activity was estimated. For purpose of directed search of polymeric systems of course, it is necessary to know the mechanism of polymers action on the development of living systems. We were interested in seed properties, cotton seeds in particular. To the beginning of our investigation we revealed the absence of the such works, namely on the polymer influence on growth and development of plant seeds. The experiments for many years allowed us to elucidate the mechanisms of polymers action on the processes, being in the base of seeds sprouting. The polymeric cover role consists of the possibility to regulate of water inflow in seed and as a consequence, the velocity of biological process, store substances hydrolysis and its products inclusion in the metabolism of germinating seed. We developed polymeric systems for seeds treatment with taking into consideration not only climate peculiarities of various regions of agricultures cultivation but also the soil types, the level of subtenanian watus. Besides the synthesis of polymers with own activity has been carried out. Such systems make it possible to regulate water flow and field germination of seeds.

With polymeric mixtures based on MC and CMC it is possible to get effects that help seeds sown early, late, and at optimal times. The use of one composition is beneficial for optimal and late sown seeds, and the use of the other is beneficial for early sown seeds. The efficiency of these systems has been determined in zones where the climate is well suited for cotton cultivation. However, most cotton cultivation occurs in Uzbekistan in the zones where climate is not conducive for growing cotton. Consequently, it was necessary to formulate the systems that would provide seed sprouting at extreme conditions of temperature and humidity. Preliminary field experiments showed that compositions based on MC and PVP proved to be effective in these extreme conditions. Seed treatment by polymeric compositions based on MC and PVP produced shoots in the northern zone of cotton cultivation. In addition, by using the changes of these components ratio, sprouting was inhibited or fastened. That gave a chance to develop of polymeric system formulating that would be beneficial in southern zones of cotton cultivation. We have also formulated polymeric systems based on PVP and CMC for long ago irrigated and newly developed land.

Chitosan has all necessary complex of properties for its use as polymeric carriers with own

biological activity. In the course of its introducing in cellulose derivatives solution jointly with microelements and growth regulators it is possible to increase seeds germination and to protect young growth against of harmful phytopathogens and on the whole to get high harvest. Chitin and chitosan in present time are widely used for cotton and rice capsulation as an polymeric system possessing its own biological activity without of chemical means of plant protection addition. The influence of chitoasn on germination energy , laboratory and field cotton seeds sprouting. The positive influence of nanopolymeric systems on chitsan base on seeds sowing qualities. It has been shown, that in different farmer economies in fergana and Namangan regions the part of raw cotton harvest of the first harvest as compared to control variants was significantly higher in the variant of cotton seeds treatment with chitosan and nanopolymeric mixtures. Thus nanopolymeric mixtures on the base of polyvinyllactame binding, chitosan and cellulose derivatives allow to increase the seeds sprouting and besides these systems possess own biological activity protesting young growth of phytopatogens action. It is necessary to get of full value healthy young growth that is the pledge of high harvest in future.

As an example it is possible to bring the systems on pectin base with polyvinyl alcohol and polyvinyl-pyrrolydone (1:1) where we reveals nanostructures formation. Seeds treatment by these systems led to crop increase on 17,8 and 6,4 c/h , accordingly.

Last time we have undertaken an attempts to incorporated new methodology in the processes of spores bioencapsulation and vegetating microorganisms which are the antogonists of microoragnisms - agents of agricultures disease.

It allows to create the preparations possessing simultaneously by growth-regulating and fungicide activity. We consider, that it will be perspective biological method of fight in the region. The significant practical problem remains elements extraction from ores with polymers used in this process. This problem is solved jointly with the Institute of Microbiology and effective polymeric systems are chosen.

Obtaining of selective polymers feed media to microorganisms cultivate which can participate biotechnological processes is very perspective. As seen from experimental data: polymer p-2 promotes microorganisms agglomeration on dispersed ore increasing the common quantity of bacteria on ore pieces in 25-37%; addition of p-2 polymer in leaching solution increases gold extraction to 8-10%.

Conclusions

It seems very perspective to obtain the selective polymeric feeding media for microorganism cultivation which may to participate in the biotechnological processes.

The investigations which were carried out on the possibility of nanoparticles formation- and nanostructures creation on the base of water soluble polysaccharide derivatives and their mixtures with synthetic polymers open great possibilities of these nanostructures polymeric materifls use in the various spheres of agriculture and biotechnology.

All above mentioned works are directed on obtaining of new polymeric systems with specific properties and activity. They have been obtained with the use of new technological approaches-nanotechnology, technology of green polymers and biotechnologies.

References

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