

MODIFICATION OF POLYMER MATERIALS – SOME FUNDAMENTAL AND APPLIED ASPECTS

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The results of theoretical and applied research in modifying fibrous and film materials which had been conducted at the department of technology of chemical and nanomaterials in recent years are summarized

Keywords: polymer materials; modifying; chemical fibers; graft polymerization; reactions of functional groups; fluoroplastics; derivatives of chitosan; composition biologically active polymers

One of the most effective methods of directional modification of composition, structure and properties of polymers are processes that are based on their chemical modification. Research in behavior of the course of chemical reactions in polymer systems, influence of fine peculiarities of macromolecule's composition, supermolecular structure on physical and physicochemical properties is one of the most important problems of the modern polymer chemistry; solving these problems provides not only development and deepening of fundamental knowledge, but also is a basis for development of methods and technological processes for production of new highly efficient polymer materials.

Reactions of graft polymerization of ionogenic and nonionic monomers containing reactive functional groups, and their subsequent chemical conversions allow to obtain modified fibers with a wide range of properties of different types of monomers, good level of retention of physicochemical properties and high processibility.

Efficient [1] reduction-oxidation systems (ROS) have been developed which enable to carry out graft polymerization of ionogenic monomers with 70...90% conversion and 90...95% efficiency of grafting, and that of nonionic up to 98 and 100% accordingly. Significant acceleration of the macroradicals formation process, when small amount of nanosized components of ROS (variable-valence metal ions) are added, has been demonstrated.

Structural and physical properties (orientation and crystallinity degree) and polymer's molecular dynamics have effect on kinetics of radical graft polymerization to oriented polymers at the boundary of solid and liquid phase. Concepts regarding the role of gel effect were extended, participation of primary low-molecular radicals in the reaction of growing chain termination was shown. Research of graft copolymers by means of chemical and physical methods (electronic magnetic resonance, proton magnetic resonance, nuclear magnetic resonance of high resolution in solid phase, IR-spectroscopy) enabled to determine the connection points of graft chains to macromolecules of polycapramides, hydrocellulose and polyvinyl alcohol; it also allowed to offer graft polymerization mechanisms of vinyl monomers using ROS $Cu_k - H_2O_2$ [2]. The results obtained correlate with those of the corresponding quantum-chemical calculation – break enthalpy of hydrogen atom, and with spin density and ionization potential of corresponding polymers.

It has been established that graft polymerization of glycidyl methacrylate onto polycapramide fiber due to a high degree of crystallinity degree and degree of orientation proceeds in the surface layers, while grafted polymer during grafting of glycidyl methacrylate onto hydrated cellulose fiber is distributed across the whole cross section of fiber.

Thus, chemical structure and structure of polymer fiber-matrix defines, already at the stage of obtaining chemisorbent, distribution

of ligand groups (across surface or in bulk) which has effect on the proportion of diffusion and kinetic components of sorption process.

Principles for adjustment of processes of obtaining sorption-active fibers have been established which are obtained on the basis of grafted copolymers; these principles are based on the employment of mathematical model approach of macrokinetics of chemical processes [3]. Equipment for the technological process and normative and technical documentation have been developed which are needed for organization of production of sorption-active fibers on the basis of grafted copolymers; the last ones have been tested under pilot conditions.

Sorption regularity of a big heavy-metals group (Cd^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Ni^{2+}) and precious metals (Pt, Rh, Pd, Ir, Ru) in form of complex chlorides have been established. Influence of constitution and structure of amine-containing sorption-active fibers on the kinetics of the process and the quantity of metal ions to be sorbed resulting from flexibility of chains containing ligand groups and their distribution in the polymer matrix have been revealed [4]. Stagewise process for purification of sewage from heavy metal ions up to the maximum permissible concentration value has been developed.

Increasingly greater attention is paid in recent years to the extension and rational usage of natural high-molecular weight compounds under the conditions of ever-increasing anthropogenic load on the environment; first of all, these include amino-polysaccharides of chitin and chitosan which are called polymers of the 21-st century.

Strong interest for chitosan and its derivatives results from a set of valuable properties and multifold possibilities for its practical application. Solubility of these polymers in water environment eases their processing (films, fibers, granules, sponge), while biocompatibility and biological degradability decrease ecological problems of their usage in such critical areas like medicine, pharmaceuticals, food industry, as well as in utilization of wastes. These polymers are susceptible of structural and chemical modification (hydro-

phobization, cross-linking, complexing); this fact enables to consider them as models for studying the processes which proceed in living matter, particularly in inter-polymer reactions with participation of polysaccharides, proteins and lipids [5].

The fundamental research performed enabled to develop improved methods for obtaining heparinoide of sulfate chitosan [6], heparinoide of sulfate chitosan [7] and its modifications (method has been successfully tested in production test conditions, preclinical trials have been carried out), carboxymethylated derivatives of chitin and chitosan [8], as well as chitosan-containing polyelectrolytic complexes, films, granules and filaments [9] which are of interest as separating membranes, efficient sorbents and drug carriers, and surgical filaments (sutures).

One of the most important research activities of the recent period is obtaining and investigation of new water-soluble chitosan derivatives— oligoethyleneoxidesulphonate chitosan (OSCH), carboxyoligoethyleneoxidesulfonate chitosan (COOSCH) and N-salts sulfooligoethyleneoxidecarboxilate chitosan, containing oligomeric nano-size non-micelle-forming SAS (ion-attached to chitosan aminogroups), which unlike the previously used SARs possess high-degree hydrophilic property and are non-toxic [10].

In contrast to solutions of acetate chitosan, the obtained derivatives produce in water neutral colorless and viscous liquids. Presence of two types of acid groups (sulfa and carboxyl) in the modifying reagent enables to obtain water-soluble derivatives with a lower degree of substitution (0.5 against 0,75 for OSCH). Films produced from liquids of new chitosan derivatives possess high elastic properties (elongation at rupture more than 40%) and sufficient strength which are used, for instance, as wound coverings (ultimate tensile stress 20...40 MPa).

In studies of surface characteristics of synthesized chitosan derivatives, dependence of surface tension and accordingly that of solutions with foaming property from solution concentration, type of the inserted substituent and molecular mass of initial chitosan has been revealed and conditions for obtaining

stable foams have been determined. Application of synthesized derivatives becomes promising thanks to the level of these obtained characteristic in the capacity of ecologically harmless emulsifiers and stabilizers of cosmetical and pharmaceutical products, food products and film-formers, as well as in foam-building technologies for finishing of textile materials.

The way from development of biologically active polymers to their introduction is complex and long; this is related to carrying out of medical-biological and toxicological tests *in vivo* and *in vitro*. One of possible methods to shorten this way – usage of already licensed medical substances during development of new pharmaceutical forms on polymer basis. The main principle, implemented in the studies, aimed at development of biologically-active ligation materials was related to realization of such interactions between components which do not result in formation of by-products effecting toxic properties of final products. Thus, varying the composition of the system provides vast opportunities for targeted design of supermolecular structure of polymer matrix containing drug substances (e.g. ferment and/or antiseptic) that determines the level of biological activity. So, when designing materials with combined biological activity [11...13] by means of applying a polymer composite layer on the fibrous matrix, strength of its fixation and stability of ferments are adjusted due to additional cross-linking by means of cross-linked reagents or insertion into the fiber structure with high degree of specific internal surface. Where it was necessary to increase the availability of the ferment, its localization in the external layers was realized by mean of application of the appropriate polyelectrolyte. Control of desorption speed of polycationic antiinfective chemical was carried out by changing its ionization degree. The fibers containing a biologically active composite material may be obtained on the basis of continuous process scheme [14].

Film materials for medical purposes on the base of polyvinyl alcohol have been developed, which are of great interest as most promising wound coverings into composition

of which different medical drugs have been added [15...17].

Influence of interactions in the system (complexing, cross-linking) on the polymer structure has been demonstrated; this enabled to produce films having a layer-porous structure with even distribution of pores or a monolithic structure with bioactive substances which are predominantly located in the external layer.

Wide practical application in different spheres, such as: during production of protective clothing for workers having contact with acids, mineral oil, lubricants, pest-killers, rescue workers of Emergencies Ministry who work under extreme conditions, for military and camouflage special clothing, fabric of suit, raincoat, furniture range, artificial fur, carpets and floor coverings find textile materials with anti-adhesive oil-, water-, acid-, mud-resistant properties.

With the aim to solve the problem of developing such new generation materials, process of synthesis of new types of polyfluorine alkyl acrylates (PFAA) from monomers have been studied, which had been synthesized for the first time by PiMinvest JSC; they are characterized by a length, structure and degree of branching of fluorine alkyl radical [18]. The research of kinetics of radical polymerization of FAA in a block and in a solution has revealed the autocatalytic character of polymerization processes which is common for all monomers investigated.

For the first time, in carrying out polymerization of 2-perfluoropentoxytetrafluorine - propyl acrylate in emulsion with varying content of anion-active SAS C-10 (latex LFM-N), the possibility for 100%-conversion of monomer without formation of coagulum with the SAS-14% concentration and above has been found.

Models of polymer chain fragments have been designed and values of steric energy level of values of PFAA have been computed with the aid of computer-aided simulation; this made it possible to arrive to a conclusion regarding increase of structural stress with the increase of total quantity of atoms in perfluoroalkyl radical and regarding presence of branching in it. Some increase of critical sur-

face energy is typical for polymers of this type.

It has been established that maximum reduction of wetting ability of modified filaments - when using PFAA with alkylene radical of linear structure - is observed for the polymer with 8 perfluorinated atoms. This for the first time established fact testifies that it is not advisable to use polyfluorine acrylates with very long fluorene alkylene chain for modification of fibrous materials.

One of the ways for adjustment of latex particles' structure, which provide for increase of property level in modification and consumption reduction of expensive fluoroorganic preparation, is to obtain latex with composite particles composed of PFAA and non-fluorinated polymers. Industrial latex materials SKD, SVCH, BNK, and SKF-32 were used as additives to latex LFM-N. If these polymers are mixed, disperse systems with particles of the type "nucleus-envelope" are formed. With postprecipitation on the surface of fiber they are able to orient themselves with the hydrophylic part to the fiber, and with the hydrophobic one - away from it; that results in formation of a closely packed layer of macromolecules and reduces significantly the surface energy of the modified material [19].

The possibility of directed regulation of colloid-chemical properties (particle size, electrokinetic potential and electrical conductivity) by changing the mixing ratio of latex LFM-N and BNK has been demonstrated, in addition, also by means of changing the type of surfactant and introduction of electrolytes or other additives [20]. Interaction potential energy of particles of compounds LFM-N and BNK with viscous fiber in the dispersion medium was computed. Optimum ratio of components in the composition on the base of latex mix of LFM-N and BNK has been determined (80:20) which enables to reach higher levels of oil-, waterproof properties of viscose rayon fiber (modified with composite latex) in comparison with finishing by particular LFM-N.

It has been established that efficiency of PFAA latex usage for surface modification of fibers is significantly influenced by reduction

of latex particle sizes (especially up to a nano-size level). In this case, uniformity of polymer film is improved which is deposited on the fiber surface; by doing so, the level of antiadhesive properties of modified materials is significantly increased too [21]. Methods for producing of PFAA nanodispersions have been proposed. One of such methods is mini-emulsion polymerization of fluorinealkylacrylates which enables to obtain dispersion systems with particle sizes belonging to nonorange (~ 40 Nm).

CONCLUSIONS

1. Some regularities of modification processes for polymer materials by means of graft polymerization, chemical transformations of functional groups in polymer chains, as well as creation of compounds with different compositions have been considered.
2. Dependence of functional activity of synthesized compounds on peculiarities of their structure and topochemistry of modification processes have been determined.
3. Promising trends for practical usage of modified materials have been discussed.

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