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Polysaccharide-based polymer blends: Methods of their production

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Abstract The existing methods of preparing polymer blends of cellulose, chitin and chitosan with natural and synthetic polymers and their applications are reviewed. The methods of solid-phase blending of these polymers under conditions of joint action of high pressure and shear deformation are discussed. Normally, under these conditions the processes of dispersion of polymer particles, amorphization, mixing at different levels, depolymerization as well as a chemical interaction resulting in formation of branched and crosslinked structures can take place. The probability and intensity of these processes depend in many respects on the type and magnitude of the external force, but the properties of the polymers are of higher importance. The advantages of the method of joint action of high pressure and shear deformation compared to the conventional techniques of polysaccharides mixtures production are shown.

Keywords Cellulose · Chitosan · Blends

Introduction

The binary blends of natural polysaccharides (cellulose-chitin, cellulose-chitosan) and their blends with synthetic polymers are the promising systems for creating of polymer materials. These blends are interesting materials for producing composite polymer films, sponges, hydrogels, ion exchangers and complexing agents, membranes, dressings, shells for encapsulated drugs, sutures, etc. The physicochemical and mechanical properties of such blends are determined by the type of bonds between the components, their compatibility, and the features of a forming supramolecular structure.

Cellulose and chitin are the most widespread natural polysaccharides, which perform structure-forming functions in flora and fauna, respectively. Unlike cellulose and chitin, the product of chitin deacetylation—chitosan contains ionogenic primary amino groups which endow it with polycationic, chelating, and other properties, as well as with the solubility in acidic aqueous media that enlarges the practical applications of chitosan and facilitates its processing [1,2].

The growing interest in recent years in chitin and chitosan has resulted in the publication of many studies on production and investigation of properties of the blends of these polysaccharides with other natural and synthetic polymers. As the physicomechanical properties of chitin and chitosan are relatively weak, the problem of their modification by mixing with synthetic and natural polymers is very important. The introduction of synthetic polymers improves mechanical characteristics of chitosan products and their stability in acidic aqueous media; moreover, these additives make it possible to reduce the product cost—an important goal. The presence of polysaccharides confers biocompatibility and biodegradability to such compositions, enhances their hydrophilicity and colorability.

Cellulose, chitin and chitosan blends with synthetic polymers

Polysaccharides containing high-polarity groups can form hydrogen bonds with the corresponding functional groups of synthetic polymers that, in turn, leads to their enhanced compatibility to each other; the synthetic polymers capable

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of hydrogen bond formation include polyamides, polyesters, and many vinyl polymers.

However, the tendency of these components to self-associate often hinders the interaction and compatibility of polysaccharides with a second polymer component. Thus, cellulose blends with poly(4-vinylpyridine) are homogeneous at any component ratio [3], and cellulose-polyamide blends are heterogeneous two-phase systems [4]. The homogeneity of cellulose-poly(vinylpyrrolidone) blends can be attained with no less than 40% content of the latter polymer [5]. The optimum compatibility of cellulose with poly(vinyl alcohol) manifests itself at 60% content of poly(vinyl alcohol) (PVA) in the blend [4]. The films from chitin-PVA blends in dry and wet state surpass the films from individual polymers in mechanical properties. In these compositions the degree of crystallinity of chitin decreases and a mixed crystalline structure is formed [6].

Polymer compositions based on polysaccharides can be produced by different methods. Thus to obtain molded products, the blends of chitosan with poly(acrylic acid) have been prepared by the method of polycondensation filling, whereas chitosan-epoxy resin blends were produced using of cold and hot curing [7]. However, the most widespread method for producing polysaccharide-based composites is film preparation from solution in the common solvent. Both cellulose and chitin are rigid-chain polymers infusible and insoluble in the available solvents. The basic problem of blend preparation with the aforementioned polymers is to find an appropriate solvent capable of dissolving both polysaccharide and second component without decomposition. In this case the problems of solvent regeneration and decreasing discharges of toxic effluents are of importance. The NO_2-dimethylformamide mixed solvent used in [8] meets these requirements only partially and films prepared from a cellulose-poly(acrylic acid) blend using this solvent retain transparence up to 50% content of poly(acrylic acid) in the blend. However, in this case, too, X-ray diffraction analysis of the films shows the presence of two crystalline structures and, hence, a reduction in components compatibility at the molecular level.

Normally, chitosan soluble in acidic aqueous media is easiest to be mixed with water-soluble polymers, such as poly(vinyl alcohol) [9–12], poly(ethylene oxide) [13–16], poly(vinylpyrrolidone) [17,18], and some polysaccharide derivatives. As is shown in [12], the films with poly(vinyl alcohol) content up to 20 mol % are transparent and have higher strength and plasticity compared to pure chitosan films. According to X-ray data, these films show a microheterogeneity and contain crystalline regions of both poly(vinyl alcohol) and chitosan. Poly(vinyl alcohol)–chitosan films can be used as fiber optic sensors for determining ethanol concentration in aqueous solutions [19] and as selective membranes [20, 21]. The study of chitosan–poly(ethylene oxide) films prepared by thermal curing of mixed acetic acid solutions of the polymers showed that the films containing 25, 50, and 63% chitosan have respectively a continuous homogeneous, a transient or a heterogeneous structure [14]. Chitosan and poly(vinylpyrrolidone) can be mixed at the molecular level in a wide range of ratios a finding which was confirmed by the data from differential scanning calorimetry, differential thermal analysis, and wide-angle X-ray scattering.

The products of mixing and interaction between the polybase chitosan and polyacids in aqueous solutions—polyelectrolyte complexes, are of special interest. Chitosan as a polycation can be used for preparing polyelectrolyte complexes with polyanions, such as poly(acrylic acid), poly(galacturonic acid), alginic acid, pectin, glutamic acid, collagen, and xanthan [22–29]. The films of polyelectrolyte complexes are usually prepared by drying mixtures of solutions of oppositely charged polyelectrolytes in volatile acids or bases followed by thermal treatment and hydrotreatment. A partial crosslinking of polyelectrolyte films occurring upon these processes results in their improved stability in alkaline and acidic media and extends the area of their practical applications.

The films of interpolyelectrolyte complexes of chitosan and poly(acrylic acid) show sufficiently high mechanical characteristics along with good transport properties and high dialysis permeability relative to low-molecular-mass water-soluble compounds that renders these films promising materials for separation, particularly, of water—alcohol mixtures [30,31]. As is shown, the membranes based on chitosan-carboxymethylcellulose mixtures have improved mechanical properties [32,33].

In recent years, studies on creation of polymer complexes using chitosan as a nontoxic biologically active carrier for drugs and other biomedical materials have been pursued very intensively [34–37]. This is especially true for production of drugs of prolonged action with controlled drug delivery [38–41]. The microcapsules made from complexes of chitosan and sodium alginate are used for immobilization of bacteria, living cells or activators and regulators of drug therapy [42,43].

A chitosan-gelatin combination facilitated generation of swelling hydrogel networks which release the incorporated drugs into the surrounding phase [44], whereas a hydrogel composition of chitosan and poly(ethylene oxide) can be used for a specific introduction of antibiotics into the stomach [45]. The stable gels, which are able to retain up to 65–95% water were prepared by complexation of chitosan with xanthan [46,47]. The above complexes can be also used for enzyme immobilization. The complexes of chitosan with hyaluronic acid are successfully used to develop coatings for wounds and burns [48,49].

At the same time, the compositions of chitosan with synthetic polymers are used as polymeric carriers; for example, a composite matrix of chitosan-poly(vinyl acetate) can be used as a carrier for aspirin-heparin drug system [50].

Cellulose—chitin and cellulose—chitosan blends

The similarity in chemical structure of cellulose, chitin, and chitosan determines fundamentally their compatibility and makes it possible to prepare homogeneous blends combining the unique properties of chitosan and the availability of cellulose. Materials based on these two polysaccharides in the form of powders, granules, gels and films can also be applied as sorbents and drug carriers. As is known, introduction of amino groups, which are more reactive than hydroxyls, into cellulose is a rather difficult problem and so cellulose—chitosan blends represent alternatives to amino derivatives of cellulose. Due to the high adhesiveness of chitosan to cellulose [51], even addition of relatively low amounts of chitosan to cellulose-based paper and textile products allows one to increase significantly their mechanical strength, colorability, bactericidal properties, and other characteristics [52].

One of promising practical applications of cellulose–chitosan blends is their processing in films, having along with high strength parameters also good biocompatibility, biodegradability and hydrophilicity. Thus, the films prepared from cellulose—chitosan blends (10–20% chitosan) are strong, yet completely biodegradable in soil within two months [53].

As demonstrated by Hasegava et al. [54] the strength parameters of films obtained from the blends are higher than those calculated by the additivity rule from the components' ratios and the maximum values of these parameters are achieved with a chitosan content of 10–20%. These results and also the data obtained upon studying Langmuir-Biodgett chitosan—cellulose films [55] confirm that cellulose and chitosan do indeed interact intramolecularly.

The choice of a common solvent to prepare films from polysaccharide blends is also a very important and difficult problem. Thus, cellulose-chitosan films have been formed from polysaccharide solutions in trifluoroacetic acid [56] and chloral-dimethylformamide mixed solvent [53], whereas cellulose-chitin films have been prepared from solutions in a dimethylacetamide-LiCl mixture [57,58]. The thermodynamic compatibility of the chitin and cellulose was studied thoroughly by the methods of the D_2O sorption by the films of these polysaccharides of various compositions and the small-angle neutron scattering. It was shown that the structure of the films changes from homogeneous to microheterogeneous with increasing content of the second component and the maximum compatibility is inherent to blends containing small (up to 2.5%) additives of the second component.

However, even the successful choice of the common solvent does not allow one to obtain the polymer concentration in mixed solutions higher than 2-5 wt % depending on molecular mass of polysaccharides. Hence, the preparation of polysaccharide-based compositions without solvent is an important scientific and practical problem.

Solid-phase method of polysaccharide blends production

Solid-phase processes of preparing blends and various derivatives of polymers are of interest, particularly, because of their higher ecological safety. [59]. One of the promising methods of solid-phase modification of polymers is the joint action of high pressure and shear deformation on the blend of solid components. Under these conditions, the reacting material is in fact subjected to plastic flow with an unlimited strain [60]. The main results of the studies of various chemical transformations induced by the joint action of high pressure and shear deformation were summarized in [61]. These processes are distinguished by the following features: (1) when reaction between solids at high pressures combined with shearing are conducted, very effective mixing of the reagents takes place on a molecular scale, required for the occurrence of the reaction, in spite of the fact that initially, both reacting compounds were solid powders; (2) under such conditions, various chemical reactions may occur with very low activation energies; that is, the reactions do not require a thermofluctuational energy supply. For solid-phase modification of individual polymers and their blends the devices which make it possible to achieve the joint action of high pressure and shear deformation are used. Blending of polysaccharides was performed using two types of equipment: Bridgman anvils (the pressure from 1 to 50 GPa) allowing to work with milligrams of reactants [62] or a twin-screw pilot extruder (Berstorff, Germany) with heating control which provides the pressure of 0.2–10 GPa and shear stress of 0.3–3 N/mm^2. Chemical modification and blending of polymers in extruder reactor in detail are discussed in [63]. In this review the influence of the times of blending and chemical reaction passing, as well as the residence time of the system in the extruder reactor on the reaction kinetics and the structure of the produced materials are analyzed. Also the most important directions of research into the chemical modification and blending of polymers are noted.

The mechanochemical modification of polysaccharides and their blends was also successfully carried out in the presence of liquid media [64], but the modification of solid polymers is of special interest. The solid-phase modification of polysaccharides under conditions of shear deformation allows one to combine the activation stage (amorphization, increasing of specific surface area and degree of dispersity) and the chemical reaction itself (the interaction with other reagents) in the absence of liquid media (solvents and diluents). The absence of the latter components not only improves the economical and ecological characteristics of the process, but provides extremely high concentrations of reactants and reaction rates.

For example, the solid-phase reaction of alkaline deacetylation of chitin and synthesis of chitosan can be successfully performed with a significantly smaller excess of sodium hydroxide for 3–5 min [65]. The interesting results were obtained upon studying the possibility of simultaneous chitin deacetylation and blending chitin, cellulose, and sodium hydroxide under joint action of high pressure and shear deformation [66]. In the reaction mixtures of this type, cellulose is present as an alcoholate and acts as an additional catalyst of chitin deacetylation reaction. The resultant chitosan represents an active molecular system and the process of its blending with the second polymer component occurs intensively with formation of versatile and stable adhesive bonds. This method of the process realization is technologically simpler and cheaper than the method of successive chitosan deacetylation and its blending with cellulose. Moreover, the presence of cellulose hinders the interpacking of chitosan macromolecules and thus improves the sorption properties of the resulting compositions.

Generally, upon the mechanical treatment of the cellulose—chitosan solid blend, the processes of polysaccharide particles dispersion, amorphization, mixing at different levels, and depolymerization are accompanied by a decrease in molecular mass, as well as by chemical interaction resulting in formation of branched and crosslinked structures, can occur. The probability and intensity of these processes depend in many respects on the type and magnitude of the external force, but the intrinsic properties of the polysaccharides are of greater significance.

As is shown, the grinding of a chitosan—cellulose composition in an extruder results in a much more intensive comminution of the blend compared to that of individual polysaccharides. Figure 1 shows the particle size distribution of the initial chitosan and cellulose grinded separately (curves 1, 2), and their equiweight blends upon single (curve 3) and manifold (curve 4) extrusion grinding at 150°C [67]. The bimodal character of the particle size distribution in the blends after a single extrusion, which is related to a pronounced difference in the dispersivity of the particles of the initial samples of cellulose and chitosan, is retained after prolonged grinding of the blend (i.e., after passage times through the extruder). A reduction in the fraction of large particles is apparently associated with the grinding of chitosan.

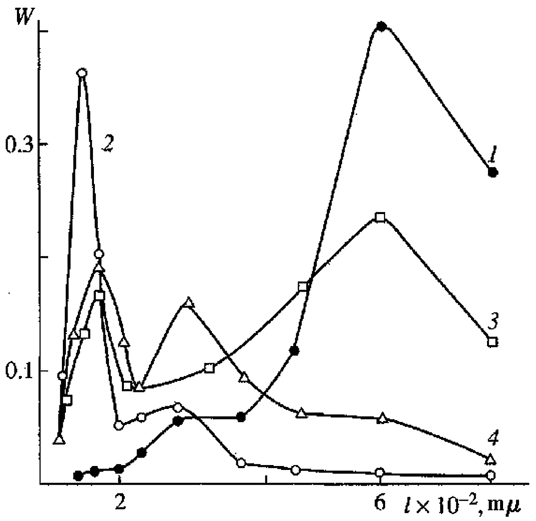

Fig. 1 Particle size distribution (W is the weight portion of fraction) for chitosan (1), cellulose (2), and their blends upon single (3) and fivefold (4) extrusion grinding at 150°C.

Upon grinding in the extruder, molecular mass of chitosan decreases from 350 to 265 kDa [68], whereas grinding together with cellulose results in a lower reduction in molecular mass (to 320 kDa); furthermore, the degree of degradation increases as the treatment temperature drops. The structural changes observed in chitosan and cellulose as a result of extrusion grinding were determined using ^{1}H NMR spectroscopy with the working frequency of 42 MHz (Table 1). The data on changing characteristics of spin-lattice relaxation T_1 and proton mobility β allowed one to conclude that, upon grinding of chitosan, the crystallite dispersion principally occurs without a significant decrease in the degree of crystallinity. This is accompanied by an increase in the sorption surface area for chitosan and, consequently, in a higher content of strongly bound water. By contrast, cellulose shows an essential amorphization. The results of measuring ^{1}H NMR relaxation indicate that, in the course of solid-phase modification of the chitosan-cellulose composition, a sharp decrease in the T_1 parameter was observed. This finding is suggestive of an increasing external specific surface area and decreasing particle size. Thus, the joint action of high pressure and shear deformation on the cellulose—chitosan blends results in intensive grinding of chitosan and amorphization of cellulose.

Table 1 Parameters of ^{1}H NMR relaxation of polysaccharides and their compositions [67]

No	Sample	T_1, ms	β,rel. units
1	Chitosan	161	0,187
2	Chitosan ground at 100°C	155	0,56
3	Cellulose	301	0,181
4	Cellulose ground at 100°C	287	0,181
5	Composition ground at 100°C	225	0,636
6	Composition ground at 150°C	194	0,8

*T_1 is spin-lattice relaxation parameter; β is index of proton mobility (the ratio of populations of mobile and immobile regions).

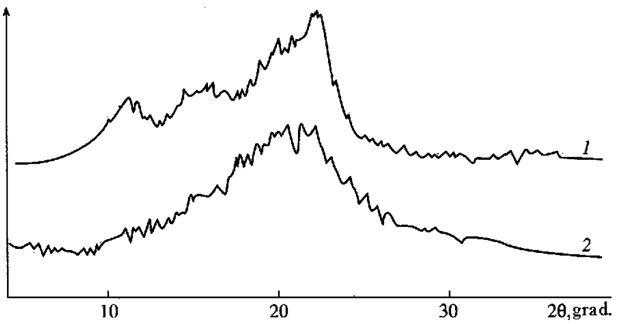

Fig. 2 Diffractograms of equiweight blends of cellulose and chitosan after (1) fivefold extrusion at 150°C and (2) treatment on the Bridgman anvils at a pressure of 1 Gpa.

X-ray diffraction analysis of equiweight cellulose—chitosan blends, after the treatment in the extruder and on the Bridgman anvils, showed that the sample treatment under more severe conditions (on the Bridgman anvils) leads to a virtually complete amorphization of the product structure even at the pressure of 1 GPa. Some reflexes, characteristic of the crystal structure of individual polysaccharides are retained at both single and fivefold extrusion (Figure 2). The pressure and shear stress increase a weak chemical interaction between two components and a qualitative change in the structure of hydrogen bonds are observed.

The films prepared by pouring a solution of acetic acid on the extruded blend show the adsorption capacity for copper ions exceeding the additive values for the components and an anomalously high rate of copper chemisorption [69]. The high sorption capacity of the films (up to 2000% in aqueous media), their good adhesion to skin, the absence of toxicity, and the possibility of drug immobilization in these films makes them potential coatings for wounds and burns. Although mechanical characteristics of the resulting films are somewhat lower compared to the films prepared from the individual polysaccharides (ultimate tensile stress 80–140 and 15–20 MPa, respectively), their strength is suitable for producing biomedical materials. In spite of structural nonuniformity of the films, the value of elongation at break, and thus their elasticity, is sufficiently high (15–30%) and can be improved by plasticization with glycerol.

Another method of chitosan-cellulose films production is using of *N*-methylmorpholin-*N*-oxide (MMO) as solvent. MMO is a solid solvent for cellulose, and in this case after grinding under conditions of shear deformation and melting of the mixture unoriented and nonhomogeneous films are formed [70]. These films possess a high swelling in water mediums (500–600%) and can essentially be of particular interest as dividing membranes or bandaging materials.

It has been suggested that the chemical interaction between cellulose and chitin in the presence of crosslinking agents and formation of a three-dimensional network improves the adsorbent stability in different media, as well as adsorption and flocculation activity of the resulting polymeric compositions. In the presence of even a small amount of curing agents, crosslinked products of both chitosan and cellulose reactions are formed. An enhancement in degree of substitution and crosslinking of the polysaccharides, for example, upon interaction with dicarboxylic acid anhydrides on the Bridgman anvils, is favored by increasing both anhydride concentration in the reaction mixture and pressure, the efficiency of anhydrides as curing agents attaining 60% (Tables 2, 3). The formation of a three-dimensional network with oligo(ethylene oxide) diglycidyl ether (DEO) as a curing agent provides an improved compatibility of the components, increased stability of sorbents in various media, as well as higher sorption and flocculation activity of the resulting polymer compositions [71].

Thus, the preparation of the cellulose-chitosan blends under the joint action of high pressure and shear deformation,

Table 2 Characteristics of the products of interaction of cellulose, chitosan, and their equiweight blends with dicarboxylic acid anhydrides and DEO in solid phase

	Reaction parameters		Gram-atomic ratio		DS calculated by		
Sample no	anhydride**, wt. %	T°,C	$C : N_{tot}$	$N_{am} : N_{tot}$	$C : N_{tot}\hat{}$	NH_2-groups	Solubility in 0.1m HCl,%
1	0	25	12.63	0.92	0	0	50
2	10	100	12.63	0.92	O	0	50
3	10	150	13.51	0.85	0.04	0.06	40
4	5	25	13.50	0.86	0.04	0.05	35
5	10	25	13.83	—	0.06	—	40
6	10	25	14.53	0.76	0.10	0.15	30
7	5	25	13.35	0.83	0.06	0.08	35
8	5	25	13.46	—	0.075	—	30
9	10	25	14.27	0.68	0.17	0.22	20

*Samples 1–3 were obtained in the Brabender mixer, samples 4–9—on the Bridgman anvils under pressure 1 GPa (samples 5 and 7) and 2 GPa (samples 4,6,8,9).

**Samples 2–6 were modified by phthalic anhydride, samples 7–9—by succinic anhydride.

Table 3 Characteristics of the products of interaction of cellulose, chitosan, and their equiweight blends with DEO in solid phase

	Gram-atomic ratio		Degree of substitution calculated with		Solubility %	
Product	$C:N_{tot}$	$N_{am}: N_{tot}$	$C: N_{tot}$	NH_{2-}	0,1M HCL	Cuprammonium complex
Cellulose-DEO	44,56*	—	0,005	—	0	68
Fraction**	44,70*	—	0,01	—	0	0
Chitosan-DEO	7,60	0,83	0,04	0,07	5,5	—
Fraction***	7,65	0,82	0,045	0,08	0	—
Chitosan-cellulose-DEO	14,36	0,86	0,03	0,05	0,5	32
Fraction	14,38	0,86	0,05	0,05	0	—

*Carbon content, wt %.

**Fraction insoluble in cuprammonium complex

***Fraction insoluble in 0.1 M HCl.

in which both the failure of the physical structure and the system transition into a mobile (plastic) state take place, allows the degrees of dispersion and blending of the components to be varied over a wide range. In this case the blending of polysaccharides occurs at the molecular level. Evidently, cellulose and chitosan can be involved in the chemical interaction, if the process is carried out under more severe conditions (elevated temperature and pressure, longer treatment time) or is effected in the presence of a third component which decreases the activation energy of their interaction. The addition even a small amount of crosslinking agents to chitosan—cellulose blends during the solid-phase modification results in almost complete insolubility of the reaction products in acidic and alkaline aqueous media. This can be explained by the formation of three-dimensional structures with multiple inter- and intramolecularly crosslinks. The insoluble chitosan-cellulose compositions are of interest as adsorbents having anion-exchange and complexing properties and are suitable for the sorption of acidic reagents, metals, amino acids, proteins, and other components.

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