STRUCTURAL AND PHYSICOCHEMICAL STUDY OF
CHITOSAN AND POLYVINYLPYRROLIDONE BLENDS

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Physical and physicochemical methods are used to study a blend based on industrial crab chitosan and polyvinylpyrrolidone over a wide composition range. Thermodynamic data indicate that this pair of polymers is compatible at certain component ratios. However, electron micrographs show that the polymeric layers are heterogeneous. The degree of heterogeneity is least at a 1:1 ratio.

Key words: chitosan, polyvinylpyrrolidone, blend, miscibility, thermodynamics, structure.

Polymer science has shown a tendency in the last decade to create blends of different polymers rather than to develop new polymers. This includes natural compounds and their derivatives [1–4]. Systematic investigations on the creation of blends of water-soluble polysaccharides and their derivatives with synthetic polymers and the evaluation of their properties have been carried out at the Institute of Polymer Chemistry and Physics of the Academy of Sciences of the Republic of Uzbekistan for several years [5-6].

In the present article, we present results from research on the structure of layers prepared from blends of chitosan (CS) synthesized from industrial crab chitin and polyvinylpyrrolidone (PVP) in acetic-acid solutions. X-ray studies (Fig. 1) showed that all layer samples, regardless of composition, produce patterns with broad maxima in the range $2\Theta = 19$-20 that are due to PVP, which has a maximum in this range. This indicates that the CS:PVP blends are amorphous.

PVP in blends with CS substantially influences the ability of the latter to crystallize. Even with a small amount of CS, diffraction maxima characteristic of CS are not evident at any component ratios.

IR spectra of CS:PVP blends with various component ratios were recorded (Fig. 2). Spectra of PVP have been described in detail in the literature. Therefore, we present only spectra for comparison with those of the blends. Spectra of the blends contain practically all absorption bands of the components. Peaks belonging to the synthetic polymer are more evident. This is probably due to the lower molecular weight of PVP compared with CS. As a result, many more macromolecules of PVP and, correspondingly, its functional groups, are contained in a unit volume of sample (Fig. 2). It is noteworthy that the broad absorption band near 1070 cm^{-1} in all compositions is absent in the spectra of the starting polymers. This band is usually identified as a C–O stretching vibration. It is very interesting that such a group exists in all studied compositions but is strongest in the 1:1 binary blends.

In general, spectra of CS:PVP blends are a superposition of the spectra of the pure components. However, (and this is especially noticeable for the 1:1 composition) several bands shift to lower wavenumbers and their intensities change. For example, the strength of the methylene stretching vibrations decreases. These changes are most evident for various deformations at 1000-820 cm^{-1}. The δ CH– deformations at 830 cm^{-1} practically disappear in the blends whereas they are clearly visible in the PVP spectra. Such changes in the IR spectra suggest a certain degree of interaction in this system.

TABLE 1. Sorption of Water Vapor (%) by Chitin, Chitosan, and PVP

Rel. humidity	Crab chitin	Crab chitosan	PVP
10	0.40	0.80	0.80
30	1.05	1.70	2.10
50	1.50	2.15	3.50
65	1.80	2.50	5.60
80	2.05	3.20	9.70
90	2.40	4.00	18.90
100	4.00	6.30	31.40

TABLE 2. Sample Sorption Characteristics

Sample	Crab chitin	Crab chitosan	PVP
x_m, g/g	0.0114	0.0154	0.0231
S_{sp}, m²/g	43.070	54.215	81.317
W_0, cm³/g	0.040	0.063	0.314
r_c, Å	20	14	77

TABLE 3. Sorption of Water Vapor (%) by Layers Prepared from CS:PVP Blends

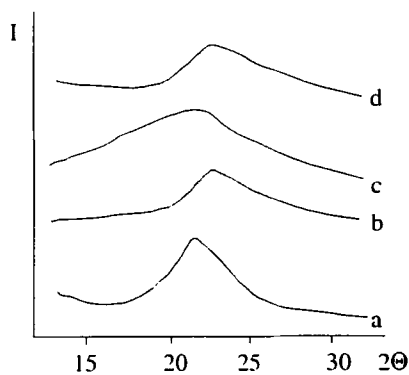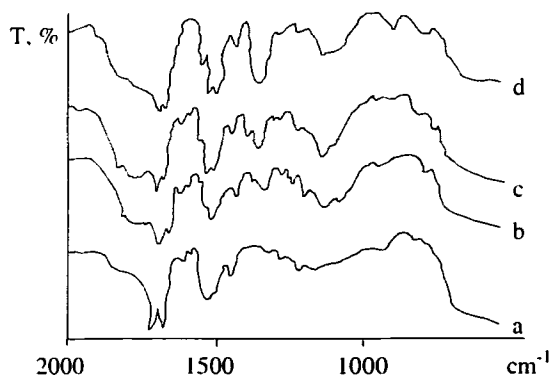| Rel. humidity	CS:PVP				
	1:1	7:3	3:7	8:2	2:8
10	0.30	0.35	0.30	0.50	0.80
30	0.70	1.10	0.90	1.20	2.10
50	1.00	1.70	1.30	1.70	3.30
65	1.50	2.40	1.80	2.10	4.90
80	2.10	3.50	2.90	2.80	7.40
90	3.10	5.10	4.20	3.80	15.00
100	5.20	9.60	7.40	6.30	25.80

Fig. 1

Fig. 2

Fig. 1. X-ray diffractograms of CS:PVP blends of various composition: industrial CS (a), CS:PVP = 3:7 (b), 1:1 (c), and 7:3 (d).

Fig. 2. IR spectra of CS:PVP blends of various composition: industrial CS (a), CS:PVP = 3:7 (b), 1:1 (c), 7:3 (d).

TABLE 4. Sorption Characteristics of Layers Prepared from CS:PVP Blends

Sample	CS:PVP				
	1:1	7:3	3:7	8:2	2:8
x_m, g/g	0.0063	0.0156	0.0118	0.0195	0.0231
S_{sp}, m^2/g	24.0951	54.740	41.520	68.665	81.317
W_0, cm^3/g	0.052	0.096	0.074	0.063	0.258
r_c, Å	43.1	35.0	35.6	18.3	63.4

TABLE 5. Thermodynamic Properties of CS:PVP Systems

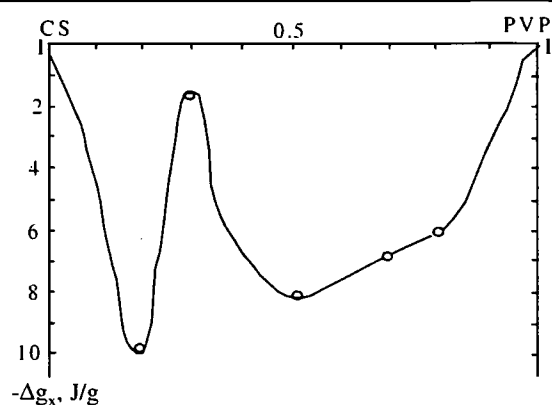| Sample	ΔG	Δg^m	$-\Delta g_x$
Starting PVP	15.3	11.75	-
Crab chitin	4.9	4.58	-
Crab chitosan	8.6	8.07	-
CS:PVP, 1:1	3.8	3.59	8.15
7:3	5.9	5.40	6.75
3:7	4.9	4.50	1.36
8:2	5.7	5.43	6.14
2:8	11.0	13.00	10.15

Fig. 3. Average free energy of mixing (Δg_x) as a function of CS:PVP blend composition.

A study of the sorption by the samples (Tables 1-4) shows that the sorptivity of CS increases compared with chitin. This is due to an increase in the hydrophilicity of CS (2.50% for CS and 1.80% for chitin at 65% rel. humidity) caused by an increase in the specific surface area and pore volume (43.07 m^2/g and 0.040 cm^3/g for chitin and 54.21 m^2/g and 0.063 cm^3/g for CS). The equilibrium sorption for the starting PVP layer is much higher than for CS. This is due to the higher hydrophilicity of PVP. The sorptivity tends to decrease as CS is added. It reaches a minimum at a 1:1 ratio and is accompanied by a substantial decrease in the specific surface area (24.09 m^2/g) and pore volume (0.052 cm^3/g). This in turn suggests a denser structure for the blend. Increasing further the CS content slightly decreases the sorptivity of the blends (7:3 and 8:2). It approaches the value for the starting CS due to an increase in the specific surface area (54.74 and 68.66 m^2/g) and pore volume (0.096 and 0.063 cm^3/g) in the samples.

Thermodynamic studies of CS:PVP systems obtained with various component ratios were carried out by static sorption. The thermodynamic miscibility of CS and PVP was estimated from the value and sign of the polymer—polymer free energy of mixing (Δg_x), which was calculated by the literature method [7].
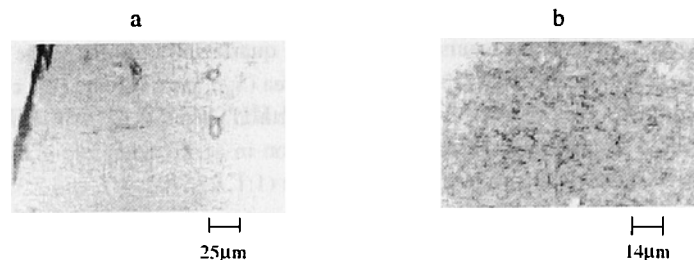
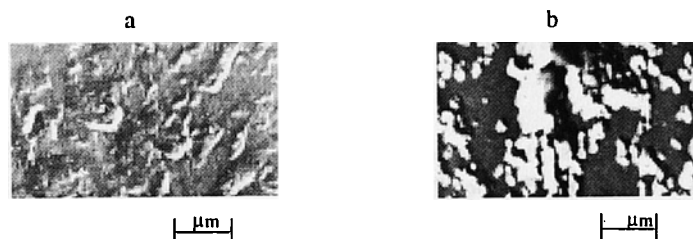Fig. 4. Optical (*a*) and SEM (*b*) images of CS:PVP blends: industrial CS (*a*) and CS:PVP = 8:2 (*b*).

Fig. 5. TEM images of CS:PVP blends: CS:PVP = 3:7 (*a*) and 7:3 (*b*).

Table 5 presents the Gibbs potentials and the average polymer—solvent (Δg^m) and polymer—polymer (Δg_x) free energies of mixing calculated from the sorption results. Figure 3 shows that the average energy of mixing of CS and PVP is negative for all studied compositions ($\Delta g_x < 0$), i.e., mixing the polymers is accompanied by a decrease of the Gibbs energy. This is consistent with thermodynamic miscibility of this pair of polymers at the given ratios (8:2 and 1:1).

Optical microscopy investigations of the CS:PVP blends (Fig. 4) showed that rather uniform layers with slight structural detail are observed regardless of the component ratio. This indicates that the components are evenly distributed in each other and suggests that this system is miscible, especially for a 1:1 ratio. SEM images show a rather uniform granulated structure.

However, greater magnifications using an electron microscope, surface samples, and ultrathin sections (Fig. 5) reveal heterogeneity, the degree of which is determined by the component ratio. Thus, surface samples from the starting PVP layer exhibit a smooth featureless surface. Adding CS causes the appearance of a very nonuniform structure at CS:PVP 3:7 as a structured surface with thin oriented and globular elements in addition to large regions of stratification.

Increasing further the CS content decreases the degree of heterogeneity, especially for a 1:1 ratio. The rather smooth surface exhibits small regions of microscopic stratification. The amount and size of these increases substantially with further increase of the CS content to CS:PVP = 7:3. This suggests that this system is immiscible. This is confirmed by studying ultrathin sections, which are smooth and structureless for starting PVP and porous and nonuniform in density for CS:PVP owing to swelling of the mixtures in the polymerized medium. The pore sizes and degree of heterogeneity increase with increasing CS content. This is characteristic of immiscible polymers.

Thus, we conclude that this pair of polymers (CS:PVP) is immiscible at the electron-microscope level, although to a lesser extent for a 1:1 ratio. The structure of the blend is less heterogeneous compared with samples at other ratios, which suggests that the physicomechanical properties of the layers are better.

EXPERIMENTAL

X-ray patterns were taken on a DRON-3M diffractometer using monochromatized Cu Kα-radiation in the range 2Θ = 10-30 . Microscopy observations were performed using a MBI-6 optical microscope a REM-200 scanning electron microscope, and a PEM-100 transmission electron microscope.

Samples were coated with silver in a VUP-4K vacuum chamber for the SEM experiments. Platinum—carbon surface

samples and ultrathin sections were prepared by known methods [8, 10] and studied for the TEM experiments.

Sorption was studied on a MacBen vacuum balance with a quartz spring in the range 0-100% rel. humidity. The sorbate was water. The volume of a monolayer (x_m), specific surface area (S_{sp}), pore volume (W_0, cm^3/g), and average effective capillary radius (r_c) for all samples were estimated using the BET method [11].

Samples were prepared as layers poured from a 2% solution in acetic acid (2%) of blends of industrial CS (90% deacetylated) and PVP (mol. wt. 10,800) at various component ratios (1:1, 2:8, 8:2, 3:7, and 7:3).

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