Perspective polymer water-soluble blends for biocapsulation. Part II

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Material and methods

We have carried out the IR-spectroscopic investigations of pure polymers and their mixtures. The mixtures have been prepared by different methods: In the form of films, casted from common solution in water; in the form of fine dispersion, precipitated from water solution in acetone and by mechanical mixing of polymers dispersion in different relations [Rashidova,1996; Burkhanova, 1989; Kalantarova, 1996; Kalantarova, 1995]. Comparison of IR- spectrum of mechanical mixture MC:PVP (1:1) with that one of film, casted from solution (for the same components ratio) has shown that in mechanical mixture all absorption bands are well defined, more intensive and narrow as compared with the film spectrum. In the last one, noticeable decrease of absorption band 1470-1420 cm^{-1}, characteristic of PVP CH_2- groups deformation band is observed. The intensity of 1380 cm^{-1} band PVP (CN-stretching) decreases and the band itself extends noticeably. Appreciable decrease the intensity of 1290 cm^{-1} band (CH_2-wagging of PVP) also observed. The absorption band at 1225 cm^{-1} (MC C-O-H or C-O-C bending) almost disappears. The bands 1165 cm^{-1} (MC ring stretching) and 1125 cm^{-1} (C-O stretching of MC) weaken sufficiently. The band at 1080 cm^{-1} (bending of C-O-C in MC) turns into shoulder. Structure sensitivity bands at 900 and 855 cm^{-1} also become weak, while the band at 790 cm^{-1} disappears completely. It is necessary to note especially that 900 cm^{-1} band intensity (CH-bending in MC methylene group) in films spectra significantly decreases, as compared with mechanical mixture. Thus IR-spectroscopic investigation of MC:PVP blends prepared by different ways, has elucidated disappearance, intensity, changes and shifting of many absorption bands, characteristic of individual polymers. We suggest that in the solution between polymers functional groups certain sufficiently complex interactions take place (H-bonding and Van-der-Vaals interactions) which are fixed in solid state. We have carried out the derivatographic investigations of MC and PVP blends, as well as their mixtures of different composition. The investigation has shown that the system 1:1 by its parameters of thermooxydative destruction differs obviously from pure components and other mixtures. The maximum of thermooxydative destruction activation energy E_a falls just on this relation (1:1) and equal to 193 J/mole, whereas for other relations these values are significantly lower. The temperature range of thermooxydative destruction and DTG maximum for the mixture (1:1) are also 193 J/mole, i.e. significantly higher for all other mixtures. It is quite probably that at this components ratio (1:1) some more strength structure is formed. In order to destroy it, it's necessary to spend more energy than for mixtures with other components ratio. It is quite clear that thermodynamic stability of system is closely connected with features of its phase condition. Therefore, we have used the method of «turbidity points» to determine the features of phase equilibrium for MC, PVP and their mixtures in water solutions. We has detected (and it agrees with literature data) that the system MC-water has lower critical temperature of solution (LCTS). For water solution of PVP with given DP we has failed to estimate CTS type due to unlimited PVP miscibility with water. Investigations of phase state of MC-PVP-water mixtures in wide range of compositions have shown that their turbidity curves are of the same type with the only feature - the narrowing of temperature-concentration regions of homogenisation with MC content increasing in mixture. The investigations

conducted have shown that system MC-PVP-water also has LCTS; which is specified MC influence in this mixture. Nevertheless it is necessary to note that when PVP content increases, the growth of LCTS is observed. The results of phase diagrams investigations fairly well agree with viscosimetry data that is characteristic of the systems possessing LCTS. The [η] of PVP water solution practically does not depend on temperature (for PVP with DP given). This correlates fully with literature data and also with the results of PVP-water system phase state. In the mixtures with PVP predominance [η] also decreases with temperature growth but not so sharply as in mixtures with high MC content. In MC:PVP mixture (1:1) the redistribution of polymers macromolecules and formation of more large structural elements than in MC solution, but smaller than in PVP solution takes place. Apparently it is connected with the formation of more strong bonds between MC and PVP macromolecules than between the same macromolecules. As a result, associates are formed, consisting of MC macromolecules existing as if they are covered by PVP macromolecules. This hypothesis is confirmed by investigations of MC macromolecules behaviour in dilute water solution and in the mixture with PVP in strong longitudinal field. It happened that addition of low-molecular PVP to MC water solution favoured to transition of MC macromolecules in uncoiled state under much more low velocity gradients than in pure MC solution. Evidently this fact confirm the partial compatibility of polymers investigated in solution, because in opposite case we could not observe the effective MC uncoiling. Thus the investigation of individual polymers as well as their mixtures of different composition in dilute and moderate concentrated water solutions depending on the temperature has shown that system MC-PVP-water has LCTS; with PVP content in mixture increases, the growth of CTS is observed. It is established that in moderate concentrated solutions of MC-PVP mixture (1:1) the associates of mixed type are formed. Very often, for theoretical prediction of polymer solubility in different solvents as well as for previous estimation of polymers compatibility, so called solubility parameters firstly proposed by Hildebrand [Hyldebrand, 1988] are used. To calculate of investigated polymers solubility parameter, different theoretical methods have been used [Van-Krevelen, 1976; Small, 1973; Hoy, 1970 (part I)]. The δ_i calculation principles according to each of methods consist in solubility parameter determination which according to Hildebrand depends on cohesion energy density by next way:

$$\delta = \sqrt{\Delta E_i / \Delta V_i}$$

where ΔE_i - cohesion energy density; ΔV_i - molar volume of polymer elementary unit.

In other methods [Van-Krevelen, 1976; Small, 1973; (part I)] instead of ΔE_i the molar constant of attraction ΔF_i are used. There, all calculations are based on the principle of values ΔE_i, ΔF_i and ΔV_i additivity i.e. the each of them may be presented as a sum of groups or atomic contributions ($\Sigma\Delta E_i$, $\Sigma\Delta F_i$ or $\Sigma.\Delta V_i$). The ΔF_i and ΔV_i values for different kinds of atoms, functional groups and intermolecular interactions have been taken from literature [Van-Krevelen, 1976; (part I)]. The polymers compatibility parameter β has been estimated by equation;

$$\beta = (\delta_1 - \delta_2)^2,$$

where δ_1, δ_2 - solubility parameters for polymers.

It is known, that two polymers to be compatible, it is necessary, as a rule, that components solubility parameter were similar to each other, as it's possible: ($\delta_1 - \delta_2 < 0,2$). Or more precisely, two polymers is assumed to be compatible if $\beta < 0,07 J/cm^3$. Koehnen and Smolders offered an in principle other method of δ calculations, where δ was considered as a sum of a three parameters: $\delta = (\delta_d^2 + \delta_h^2 + \delta_p^2)^{1/2}$. The every of components δ is found from the next equations:

$$\delta_d = 9,55n - 5,55 ,$$

where: n - refraction index, calculated from equation:

$$n = \left[\frac{1 + 2R_{LL}/V_m}{1 - R_{LL}/V_m} \right]^{1/2}$$

R_{LL} - molar refraction (the values have been taken from [Van-Krevelen, 1976; (part I)]).

$$\delta_h = \left[\frac{E_h}{V_m} \right]^{1/2}$$

where E_h - hydrogen bonding energy (its value is cited in [Small, 1973; (part I)]).

$$\delta_p = 9{,}55 - \mu/ V^{1/2} \ ,$$

where μ - dipole moment, determined from equation:

$$\mu = \left[\frac{P_{LL} - R_{LL}}{20{,}6} \right]^{1/2}$$

P_{LL} - molar polarizability, also determined from [5, report I].

All methods, above-mentioned has been used for MC and PVP solubility parameters calculations. It is necessary to note some difficulties we have met in the course of calculation. In the literature cited [Van-Krevelen, 1976; (part I)] the values of ΔE_i, ΔF_i and ΔV_i increments for a lot of groups and cycles on are absent. In this connection, in the course of calculation we was forced to separate MC and PVP monomeric units by different ways. It makes difficult δ calculation and estimation of polymers compatibility parameters. It is necessary also to stress, that additivity methods proposed by Van-Krevelen , Small and Hoy [Van-Krevelen, 1976; Small, 1973; Hoy, 1970 (part I)] does not take into account the contribution of H-bonds in total value, though for MC this contribution is significant. Besides, we have not found in any table the ΔF_i and ΔV_m values for five- and six-membered heterocycles, with N and O atoms. In this connection we was forced to take that or other values which were absent for any atoms groups, from different sources. It is why some of δ values seem overestimated or underestimated to some extent. It is well known from experimental data, that on polymers compatibility besides their nature, some more factor affect, such as molecular mass, concentration and components relation. The change of one of these factors may leads both to decline and to improve of polymers compatibility. We note, nevertheless that there are in literature a lot of theoretical data on compatibility, which coincide well with experimental ones [Hyldebrand, 1988] and theoretical method appears to be very precise. The theoretical calculations of solubility and compatibility parameters for MC, PVP and their mixtures of different composition have shown on small probability of compatibility for this polymer pair. Possibly, it may be connected to those approximations in calculation, we have mentioned above. We could not consider such factors, as solvent nature, mixture composition, temperature etc., which influence on polymers compatibility. In the same time, these data agree with fine structure investigations which has been shown the lack of true compatibility in this system. It is clear that any fundamental investigation has to be eventually realised in some spheres of man's life activity. Our investigations are not an exception. They are directed on introduction of given system as a polymeric carriers for different physiologically active substances using for many agriculture seeds treatment. In this connection to solve a lot of technological problems we have to deal with more concentrated solutions. Besides the study of viscoelastic properties of solutions gives very valuable information about their structure. The investigations of reological properties of MC, PVP and their mixture (1:1) moderate concentrated water solutions depending on temperature, have allowed to calculate the values of "viscous volume" V^* which is the measure of structural elements mobility and their dimensions in solution [Hyldebrand, 1988]. Activation energy of PVP water solutions viscous flow in studied

range of shear tension remains practically constant, whereas for MC solution decreases, but in the both cases increases with a temperature growth. This is accounted for not only by unfolding of MC and PVP macromolecules with temperature increasing, but also by intensification of intermolecular interactions. The same tendency is observed for MC:PVP mixture (1:1). As to dependencies of ΔS_b and ΔH_b on shear tension applied, their character is approximately the same for each of the initial components. However these relationships for the mixture have unusual character and are explained most probably by full MC macromolecules unfolding in presence of PVP, with simultaneous disordering of solution structure. Calculated V^* values have shown (table 1) that in PVP solution less mobile and more large structural elements are formed.

Table 1

lg, Pa	T, K	$V^* \times 10^{-28}$, m^3		
		MC	PVP	1:1
0,2	293	7,69	18,19	12,09
	303	9,62	20,77	14,21
	313	11,92	23,64	17,92
0,6	293	3,47	7,70	5,40
	303	4,46	8,77	6,52
	313	5,45	9,89	7,78
1,0	293	1,57	3,19	2,30
	303	1,95	3,61	2,70
	313	2,40	4,08	3,24
1,6	293	0,52	1,02	0,78
	303	0,64	1,16	0,90
	313	0,77	1,29	1,07

The changes of «viscous volume» V^* with temperature and shear tension for PVP, MC and their mixture (1:1) in water

Conclusions

Thus, all these data show clearly, that various methods of polymers structure compatibility estimation have led to very different and contradictory, at first glance, results. It is not surprising, because every method elucidates the structural features and polymers interaction in a mixtures on the very different structural levels. So it is difficult to expect the full coincidence of data obtained by different methods. We think, that this problem is very interesting and hope, to discuss it in detail in future.

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