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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Formation of Membranes from Aliphatic Polyamide–Polyvinylpyrrolidone Blends

O. V. Suberlyak, Yu. Ya. Mel'nik, and N. M. Baran

L'vivs'ka Politekhnika National University, Lviv, Ukraine

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Abstract—The performance of polyacrylic acid of various molecular weights and of its formulations with sodium tripolyphosphate and Na2EDTA as inhibitors of deposit formation and as dispersants was examined..

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The development of novel filtering, in particular, membrane, materials with special properties is a topical problem [1]. Particular attention should be given to the use of polymeric materials for preparing membranes for medical purposes, in particular, for dialysis [2].

It is known that aliphatic polyamides are highly resistant to alkalis and to the majority of solvents, and membranes based on them exhibit selective retaining power in baromembrane processes and preserve physicomechanical properties in a wide temperature range (up to 130°C) [2]. At the same time, in dialysis, which is widely used in medical practice, e.g., in hemodialysis, polyamide membranes are unsuitable because of their low dialytic permeability.

A promising way to increase the dialytic permeability of polyamide membranes is their modification, in particular, physical modification by blending the initial aliphatic polyamides under the conditions of their viscous-flow state or in solution with a modifier that increases the permeability, so as to preserve high physicomechanical properties of membranes. As a modifier we chose amphiphilic low-molecular-weight polyvinylpyrrolidone, which has found use in medical practice as a sorbent thanks to its nontoxicity, high hydrophilicity, and tendency to complexation with both electron donors and electron acceptors.

Among industrial processes for production of film membranes, the most widely used is membrane forming from polymer solutions. Dissolution of polymers with the aim to prepare the initial working solutions for film formation is an important step of polymer processing, determining the supramolecular structure of the polymer in the film owing to physical interaction of components in solution. The choice of the working solution concentration depends on the kind of the polymer, its molecular weight, and solvent used and determines the film formation conditions. One of the main limiting parameters governing the choice of the working solution concentration is its viscosity [3].

The goal of this study is the development of a procedure for forming membranes based on aliphatic polyamide–polyvinylpyrrolidone blends from solutions in formic acid and to determine the optimal compositions of forming solutions for preparing functionalized highly hydrophilic dialysis membranes.

EXPERIMENTAL

In our study we used poly-ε-caproamide (PA-6) with MFI = 8.67 g/10 min, copoly(hexamethyleneadipamide –caproamide) (PA-66/6) with MFI = 12.0 g/10 min, and polyvinylpyrrolidone (PVP) with MW = 12 000 ± 2000. Blending of PA and PVP was performed in solution in the course of polymer dissolution for preparing casting solutions, or in a melt by vigorous dispersion in a worm plasticizer at 230°C, with the formation of a uniform polymer blend by dissolution of PVP in the polyamide melt. The blends contained from 1 to 10 wt % PVP.

Membranes were formed by casting solutions of PA–PVP blends in formic acid containing a definite

Table 1. IR spectra of films based on PA-6–PVP blends. Casting solution composition: PA-6–PVP : HCOOH : H_2O = 7.2 : 77.7 : 15.1 wt %

Polymer blend composition, wt %		Absorption band, cm^{-1}				
PA-6	PVP	\ N–H /	–CH_2–	– N – | (ring)	pyrrolidone ring	O // –C \ (ring)
100	0	3300	2943	–	–	–
98	2	3280	2936	1293	1416	1660
0	100	–	–	1275	1424	1680

amount of water, followed by evaporation of the solvent to dryness at 80°C [4].

The mechanical properties of the synthesized membranes were evaluated by the breaking tensile stress and elongation at break, and the sorption properties, by the equilibrium water absorption W (%):

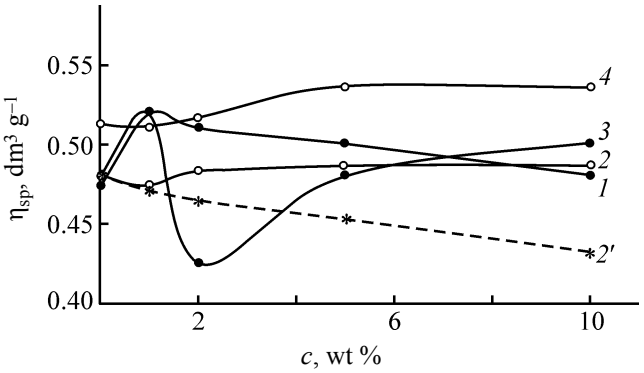
$$W = \frac{m_2 - m_1}{m_2} \times 100.$$

where m_1 and m_2 are the weights of the dry sample and of that after equilibrium swelling in water, respectively (g).

The permeability of membranes was studied in the course of dialysis of a model substance (sodium chloride) from aqueous solutions using a direct-flow laboratory dialyzer equipped with a peristaltic pump. The rate of circulation of liquid flows was 2.5 l h^{-1}. The amount of NaCl was determined with an R577 ac bridge using platinum reference electrodes. The film permeability was estimated from the salt permeability coefficient K (mol m^{-2} s^{-1}) determined from the slope (tan α) of the plot of G/S vs. τ, where G is the amount of the substance transferred through the membrane (mol); S, effective surface area of the membranes (m^2); and τ, dialysis time (s). The viscosity characteristics of dilute solutions in formic acid were determined with an Ubbelohde viscometer with a capillary diameter of 0.56 mm, and those of concentrated solutions, by the falling ball method in a Hцppler viscometer. The IR spectra were recorded with a Specord M-80 spectrophotometer in the frequency range 400–4000 cm^{-1} [5].

The viscosity of dilute polymer solutions affords information on the conformation of macromolecules and on their physical interaction with the solvent [6]. Of much interest is the dependence of the solution viscosity on the content of low-molecular-weight PVP. It can be expected that introduction of low-molecular-weight PVP into the polymeric component of the solution should cause a gradual decrease in the specific viscosity η_{sp} (according to the additivity rule, curve *2'*). However, as seen from the figure, the dependences of η_{sp} on the PVP content differ essentially from the theoretical dependence. Furthermore, these dependences are appreciably influenced by the solution preparation conditions and nature of the matrix polyamide.

When the solution is prepared from a PA–PVP blend formed in a melt, at a PVP content of 1 wt % the solution viscosity somewhat increases relative to the viscosity of



Influence of the PVP content c on the viscosity η_{sp} of solutions of polyamides (*1, 4*) PA-6 and (*2, 3*) PA-66/6. Solvent: HCOOH : H_2O = 85 : 15 wt %. (*1, 3*) Blending in a melt; (*2'*) calculated dependence; c_{PA-PVP} = 5 g dm^{-3}, 20°C.

Table 2. Dynamic viscosity of solutions of PA-6–PVP blends. Solvent HCOOH : H_2O = 83.7 : 16.3 wt %

Run no.	Polymer blend composition, wt %		μ, cP, at indicated PA-6–PVP concentration in solution, wt %		
	PA-6	PVP	5.0	7.2	15.0
1	100	0	22.0	46.9	395
2	99	1	21.4	45.4	382
3	98	2	21.0	44.5	372
4	95	5	20.0	41.9	339
5	90	10	18.5	37.8/37.3[a]	290/280[a]

[a] In 7 days.

Table 3. Properties of membranes based on PA–PVP blends. Casting solution composition: PA–PVP : HCOOH : H_2O = 7.2 : 77.7 : 15.1 wt %

Property	Composition of PA–PVP polymer blend, wt %									
	100 : 0		99 : 1		98 : 2		95 : 5		90 : 10	
	PA-6	PA-66/6	PA-6	PA-66/6	PA-6	PA-66/6	PA-6	PA-66/6	PA-6	PA-66/6
Breaking tensile stress, MPa	15	10	23	11	28	14	14	11	14	10
Relative elongation at break, %	22	29	23	45	32	51	19	25	18	45
Equilibrium water absorption, %	9	10	12	11	21	14	22	15	23	18
Salt permeability coefficient for NaCl, K × 10^{-5}, mol m^{-2} s^{-1}	3,5	1,9	0,13	1,8	2,7	3,2	6,2	3,5	27,2	12,6

the solution of pure PA-6, and at higher PVP content the dependence of η_{sp} on the PVP concentration is virtually parallel to the calculated curve. It should be noted that, when the solution is prepared by dissolving the same initial components in the solvent, the viscosity gradually increases with an increase in the PVP content in the blend. For PA-66/6, the character of changes is more complex, although the tendency of η_{sp} to increase with an increase in the PVP content (over 5 wt %) is preserved.

Such a shape of the dependence of η_{sp} on the amount of low-molecular-weight PVP introduced into a PA solution may be primarily due to intense physical interaction of PA and PVP macromolecules with the formation of interpolymeric complexes, favoring unrolling of macrochains and thus causing an abnormal increase in the viscosity.

The occurrence of complexation of PA with PVP is confirmed by the IR spectra of the films prepared from solutions of the polymers in formic acid with an addition of water and thoroughly washed and vacuum-dried (Table 1). As can be seen, in the spectra of films of PA-6–PVP blends the absorption bands of the NH and C=O groups are shifted. Most probably, the complexation occurs via hydrogen bonding. The shift of the absorption bands is indicative of the participation of these groups in intermacromolecular interactions via complexation.

The dependence of the viscosity of concentrated solutions on their composition and concentration is important for determining technologically acceptable concentrations in the course of film formation. A specific feature of concentrated polymer solutions is that the fluctuation network formed in them causes high effective viscosity, which can vary in a wide range depending on the stability of network points and strength of interaction of the polymer with the solvent.

Rheological studies of concentrated solutions in formic acid with water admixtures (Table 2) showed that the dynamic viscosity of these solutions sharply increases at a PA–PVP blend concentration within 15 wt % in the entire examined range of polymer ratios. It should be noted that, at high concentrations, the viscosity tends to decrease with an increase in the PVP concentration (in contrast to the dependence described above), with the decrease becoming more pronounced for more concentrated solutions. Based on these data, the technologically acceptable concentration of polymers in casting solutions was determined to be 7–8 wt %. The viscosity of solutions, even with a high PVP content, varies with time insignificantly, indicating that the solutions are stable and can be stored for a long time (Table 2, run no. 5).

We confirmed the possibility of controlling the dialytic permeability of the PVP-containing polyamide membranes obtained. Variation of the polymer ratio in the blend leads to a considerable change in the dialytic permeability. The physicomechanical properties of films vary insignificantly and are on a high level (Table 3). We also found that an increase in the PVP content in the blend, irrespective of the structure of the polyamide, leads to an increase in the sorption power and permeability of membranes, with the physicomechanical properties preserved. This fact suggests that membranes based on PA–PVP blends will be efficient in dialysis, including hemodialysis, taking into account high antithrombogenic activity of PVP-based materials [7].

CONCLUSIONS

(1) Physicochemical interaction of a polyamide with polyvinylpyrrolidone in formic acid solutions was proved. This interaction depends on the polymer ratio and acid concentration. It affects the physicomechanical properties and selective-transport characteristics of the membranes prepared from the solutions.

(2) Membranes based on blends of the examined polymers can be used in dialysis. Their permeability can be controlled by varying the composition of the initial polymer blend, its preparation procedure, solution concentration, and solvent composition.

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