

Miscible Blends of Polybenzimidazole and Polyaramides with Polyvinylpyrrolidone

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SYNOPSIS

The blend behavior of polybenzimidazole and a series of polyaramides with polyvinylpyrrolidone is presented. Regardless of their chemical structure, all systems showed miscible blends over the composition range investigated. This may offer the opportunity to extend the application range of these basically structural materials into the area of functional polymers. Especially in membranes, the addition of the highly hydrophilic polyvinylpyrrolidone leads to a considerable increase in performance, i.e., in flux and antifouling behavior.

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INTRODUCTION

High-performance polymers are generally distinguished from standard polymers by excellent mechanical or thermal properties.¹ In most cases, however, these exceptional material properties have been optimized with respect to structural applications. To improve their property profile for functional applications, blending with other polymers is one approach to achieve a better balance of properties. An optimum of synergistic effects may be expected from miscible blends, although homogeneous mixing of two high molecular weight polymers is relatively rare due to low mixing entropy.^{2,3}

Recently, a new family of high-modulus, high-strength fibers based on polyaramides with tensile properties similar to those of commercially available poly-*p*-terephthalamide was introduced. These polyaramides are made from terephthalic acid and mixtures of preferably three diamines and can be spun into fibers from either DMAc or *N*-methylpyrrolidone (NMP) solutions.^{4,5,6}

Polybenzimidazole (PBI) is a commercially available polymer of high-temperature stability ($T_g = 423^\circ\text{C}$), nonflammability, and high chemical re-

sistance. PBI can be spun into a fiber with excellent textile and tactile performance, exhibiting properties not found in other synthetic fibers.³

As already mentioned, there is still an ongoing interest for improvement of polyaramide and PBI with regard to functional properties such as processability, hydrophilicity, or dyeability. Therefore, investigations were started with different water-soluble polymers. Among the systems tested, polyvinylpyrrolidone (PVP) has been found to be miscible with a surprisingly large number of polyaramides and PBIs, regardless of their chemical structure. Furthermore, these miscible blends lead to new areas of applications, which cannot be met by the pure compounds, e.g., highly hydrophilic membranes or ductile films. This article deals with the preparation and the properties of some typical blends and describes one membrane application in more detail.

EXPERIMENTAL

Materials

Several polyaramides were synthesized according to procedures given in the literature.⁴ Polybenzimidazole (PBI) was supplied by Hoechst Celanese Corp. Polyvinylpyrrolidone (PVP) was purchased from BASF AG (Luviskol K30®). The structures of the polymers investigated are given in Table I to

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Table I Structures and Physical Properties of Blend Components

Abbreviation	Structure	T_g (°C)	I.V. (dL/g)
T-BAB		235	1.0
P-BAB		265	0.9
T-BABS		280	1.1
TBI-BAB		245	1.2
HMA		*	2.6
PBI		425	0.7
PVP		175	^b

* Glass transition temperature not detectable by DSC.

^b Weight-average molecular weight according to product brochure: 40,000.

gether with the corresponding glass transition temperatures and intrinsic viscosities.

Preparation of Blends

Blends have been prepared by dissolving the corresponding polyamide or PBI together with PVP in NMP at room temperature. From these solutions, films were cast and dried at 110°C in a vacuum oven (20 mbar) for 8 h followed by immersion in water for 24 h in order to remove residual NMP. An additional drying step was done at 110° for 8 h in a vacuum oven (1 mbar).

Methods

Glass transition temperatures were measured by differential scanning calorimetry (DSC, Perkin-Elmer DSC-7, 20 K/min). Apparent intrinsic viscosities

were measured in NMP at 25°C using an Ubbelohde viscometer.

Miscibility of Blends

This section deals with the analysis of the thermodynamic properties, i.e., the miscibility behavior of blends of polyamides and PBI with PVP. The analysis of the data obtained for T-BAB and PBI is discussed in more detail. These systems serve as representative examples of the miscibility behavior of all blends studied.

Figure 1 shows glass transition temperatures of binary T-BAB-PVP blends as a function of composition. In all compositions investigated, a single glass transition temperature is observed. This is a strong indication that these blends are homogeneously mixed on a molecular scale. In accordance with that conclusion, all blends were found to be

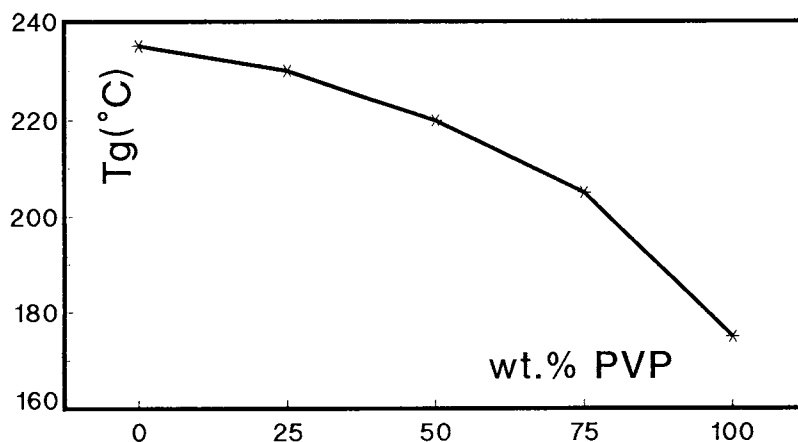


Figure 1 Glass transition temperatures of T-BAB/PVP blends.

transparent. Moreover, the glass transition temperatures of the blends are not altered after immersing the films for 6 h in boiling water.

All blends of polyaramides with PVP show transparency and glass transition temperatures comparable to those of T-BAB-PVP blends. Table II gives glass transition temperatures of blends containing 50 wt % PVP and 50 wt % P-BAB, and 50 wt % T-BABS and 50 wt % TBI-BAB, respectively.

Figure 2 displays glass transition temperatures of binary PBI-PVP blends as a function of composition. Analogously to polyaramide-PVP blends, a single composition-dependent glass transition temperature is observed. Thus, these blends, too, are homogeneously mixed on a molecular scale. This conclusion is supported in that all PBI-PVP blends were found to be transparent.

Mechanical Properties of PBI/PVP Blends

To obtain a preliminary estimate of the mechanical properties of the blends, samples were stamped out of films containing 35 wt % PVP. For this composition, an *E*-modulus of 3 GPa was measured; elongation at break and tensile strength showed values

of 4% and 70 MPa, respectively. It is important to note that films from PBI and from PVP, separately, cannot be prepared on account of extreme brittleness.

MEMBRANES FROM POLYARAMIDE/PVP BLENDS

Membrane Preparation

For ultrafiltration (UF) membrane preparation, the aromatic copolyamide termed HMA (Table I) was found to be especially well suited. A polyaramide UF membrane was prepared from a 6% w/w solution in NMP of the copolymer shown in Table I.^{7,8} The viscous solution was cast onto a nonwoven polypropylene fabric. A porous membrane was then formed via "phase inversion,"⁹ i.e., by quenching the polymer film in water. A typical UF membrane with a molecular weight cutoff (MWCO) of 20,000 g/mol resulted.

Blend membranes were prepared analogously from solutions of 6% w/w polyaramide and varying amounts of PVP (2, 3, 4, and 6%) in NMP.¹⁰ They were cast onto a fabric and then coagulated in water. Gravimetric analysis showed that more than 90% of the PVP ended up in the membrane phase, whereas less than 10% of it diffused into the coagulation water bath. Hence, it was clearly a polyaramide/PVP blend membrane that resulted from phase inversion of the ternary NMP/PVP/polyaramide solution.

General Membrane Properties

The polyaramide and the polyaramide/PVP blend membranes were transparent, indicating that the

Table II Glass Transition Temperatures of Blends of Polyaramides Containing 50 Wt % PVP

Blend	<i>T</i> (°C)	Transparency
T-BAB/PVP	215	Yes
P-BAB/PVP	230	Yes
T-BABS/PVP	210	Yes
HMA/PVP	^a	Yes
TBI-BAB/PVP	220	Yes

^a Glass transition temperature not detectable by DSC.

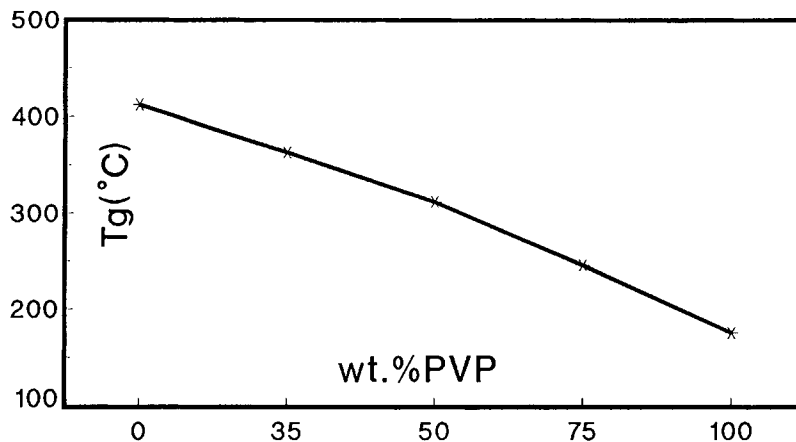


Figure 2 Glass transition temperatures of PBI/PVP blends.

active skin layer was supported by a spongy substructure with polymer aggregates and interstices smaller than the wavelength of visible light. This conjecture was confirmed by SEM analysis of the membrane samples. Figure 3 is an electron micrograph of a polyamide membrane showing part of the active surface and of the substructure. The porous support of the top layer is spongy with no fingers or voids being detectable. The spongy substructure provides a mechanically excellent, although highly porous support for the active UF skin. Adhesion of the polyamide membrane layer to the fabric, resistance toward abrasion, and pressure sta-

bility of the membranes are very good. Due to its high volume porosity of $\geq 75\%$, the spongy support is highly permeable. The polyamide membrane had a water flux of $50 \text{ L/m}^2 \text{ h-bar}$. The permeability of the polyamide/PVP blend membranes was even higher, depending on their PVP content (see Table III).

Besides mechanical stability, further material properties of the polyamides could be transferred to the membranes, namely, thermal and chemical stability. They may be used in organic solvents, e.g., toluene or chlorobenzene, even at temperatures above 100°C . Last but not least, they may be cleaned

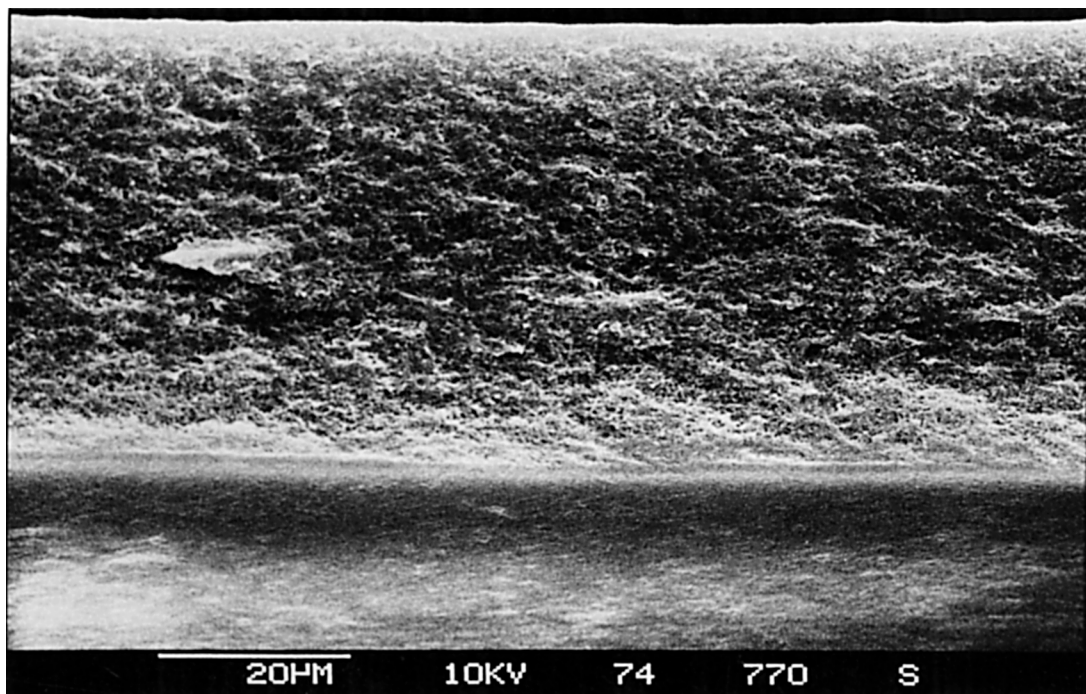


Figure 3 Electron micrograph of a polyamide UF membrane from HMA. The skin is supported by a practically void-free spongy structure.

Table III Hydraulic Permeability P_{initial} and Fouling Behaviour $P_{\text{fouled}}/P_{\text{initial}}$ for Polyaramide and Polyaramide/PVP Blend Membranes

$W_{\text{(HMA)}}$	$W_{\text{(PVP)}}$	$W_{\text{(HMA)}} : W_{\text{(PVP)}}$	P_{initial} (L/m ² h-bar)	$P_{\text{fouled}}/P_{\text{initial}}$
6	0	100 : 0	50	0.55
6	2	75 : 25	62	0.68
6	3	67 : 33	68	0.85
6	4	60 : 40	80	0.96
6	6	50 : 50	73	0.96

W = weight fractions of polyaramide and PVP in the membrane-forming polymer dope.

by the usual procedures with strong acids and bases at temperatures up to 60°C.

Fouling Behavior

Regarding practical applications of UF membranes in aqueous solutions, their fouling behavior is of utmost importance. Fouling leads to a decrease of membrane flux and thus severely limits the performance of a membrane process. Although the microscopic mechanism of fouling is still under discussion¹¹⁻¹³ and is probably slightly different for each single solute on each membrane, irreversible surface adsorption of solute and pore narrowing or blocking seem to be prominent in all cases. In most cases of practical importance, hydrophilic membrane materials showed the best results in avoiding severe fouling. One mechanistic explanation for this finding is that a steady state may be reached and complete fouling be avoided as long as water molecules are competing with solute molecules for adsorption onto the skin layer and inner surface of the membrane. This means that a steady "surface renewal"¹⁴ occurs on hydrophilic membranes while hydrophobic ones become blocked progressively and irreversibly.

Polyaramides are hydrophilic materials by their chemical nature. The amide group forms hydrogen bonds both by donating the NH proton as well as by accepting protons at the C=O group. The reason for introducing PVP as a blend partner of HMA was to improve hydrophilicity even further by this water-soluble polymer. Laboratory tests revealed that the blend membrane actually had superior fouling behavior as compared to the polyaramide membrane. Staining experiments were conducted with a dilute, colored solution of the protein cytochrome *c*. The protein solutions were ultrafiltered over both a polyaramide and a polyaramide/PVP blend membrane at 3 bar transmembrane pressure for 2 h. Afterward the membranes were immersed in a buffer solution for 24 h. Whereas the polyaramide membrane showed the intense red color of adsorbed cytochrome

c that was not removed by the buffer solution, no residual coloring was observed in the case of the polyaramide/PVP blend membrane due to desorption of cytochrome *c* into the buffer solution.

A further test was carried out as described below: A polyaramide membrane and a polyaramide/PVP blend membrane were immersed in a buffered solution of bovine serum albumin (BSA) for 24 h. Their hydraulic permeability (water flux) after this treatment, P_{fouled} , was compared to the value of the as-cast membranes, P_{initial} . Table III gives a comparison of the hydraulic permeabilities of the native membranes, P_{initial} , and of $P_{\text{fouled}}/P_{\text{initial}}$ for the polyaramide membrane and polyaramide/PVP blend membranes with different PVP contents. The value of $P_{\text{fouled}}/P_{\text{initial}}$ reaches its maximum value of > 0.9 at amounts of PVP relative to polyaramide of ≥ 0.66 . For hydrophobic membranes, it may, however, be as low as 0.10.

Hence, a superior, hydrophilic UF membrane combining the advantageous chemical, thermal, and mechanical properties of aromatic copolyamides with the high water uptake of PVP resulted from a miscible blend of both polymers. Due to its combination of properties, the membrane may be used in applications where conventional membrane materials fail. One example is biotechnology, where cellulose derivatives, being the bench mark as far as hydrophilicity and fouling behavior are concerned, can hardly be used: In most cases, the cellulose derivatives do not withstand microbial attack and disintegrate rather quickly. A plot of the permeate flux vs. operation time during the work up of a fermentation broth is shown in Figure 4. The polyaramide blend membrane clearly shows superior permeate flux as compared to polysulfone membranes, even if a polysulfone membrane with much higher nominal MWCO and pure water permeability is used.

Other examples in typical heavy fouling environments, e.g., UF of drainage water from landfill sites, demonstrated that hydrophilicity and fouling behavior of the polyaramide/PVP membrane is com-

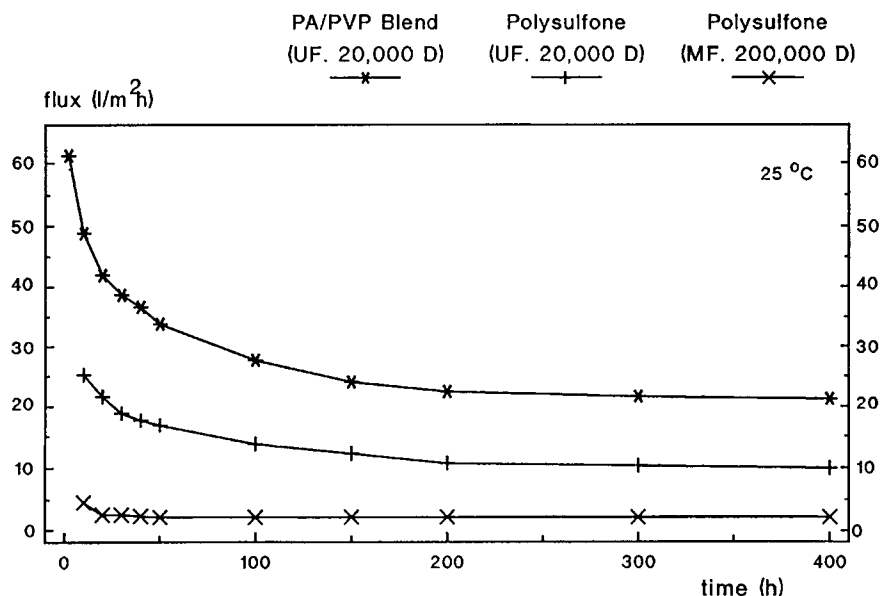


Figure 4 Product permeate flux as a function of operating time as measured for a work up of a fermentation broth.

parable to membranes of cellulose and cellulosic esters. Cleaning and sterilization of the PA/PVP blend membrane was, however, much easier because of the cellulosic derivatives becoming hydrolyzed at moderate pH's and low temperatures.

CONCLUSIONS

Surprisingly, some polymers with heterocyclic nitrogen-containing moieties or amide linkages are fully miscible with PVP. This has been demonstrated by a PBI and a number of polyaramides. With this additional degree of freedom in polymer modification, the application range of PBIs and polyaramides, so far limited to fibers, can potentially be easily and inexpensively increased. One example of great practical importance is the improvement in hydrophilicity of UF membranes. As an example, a membrane made from a polyaramide/PVP blend shows a uniquely balanced property profile: chemical and thermal resistance with high flux and low fouling behavior. This property profile is currently not met by any other commercially available membrane.

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