

Polymeric Alloys of Poly(vinylpyrrolidone) with a Macrocylic Polyether-Polyamide

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Synopsis

High molecular weight polyamide (PC-6) with macrocyclic polyetheral rings incorporated into the polymeric backbone was synthesized by a modified interfacial polycondensation of isophthaloyl chloride with diamino-dibenzo-18-crown-6. The high molecular weight polymer is a good film-forming material and forms homogeneous blends with poly(vinylpyrrolidone) (PVP). Scanning electron microscopy did not reveal any heterogeneity in such blends. The water-soluble PVP is not leached out from the blends even after a prolonged storage in water. Excellent mechanical properties of PC-6 were not adversely affected by blending it with PVP. The thermomechanical analysis and differential scanning calorimetry of the blends showed a single transition in lieu of those of the two components. PVP was also found to exert a stabilizing effect on the polyamide. The blends have been found to be thermally more stable than their components.

INTRODUCTION

Blending of polymers represents an established approach to the problem of modification of properties of polymeric systems. An intimate blending of the polymeric components may be unimportant or even undesirable in some cases (e.g., high-impact polystyrene). However, in various applications involving films or fibers it may be mandatory.

The entropy gain due to the mixing of polymeric molecules is negligible,¹ and consequently the compatibility of polymeric components is quite limited. Indeed, only a few polymeric mixtures were recognized as "true" blends.² Such mixtures are sometimes referred to as "polymeric alloys" or interpolymers.³⁻⁵ In polymeric alloys, the entanglement of the two polymeric networks may act as quasi-crosslinking. Hence, their solubility characteristics may be different from those of the individual components, e.g., organic polyphosphonates are soluble in aromatic hydrocarbons, but they are not leached out by them from their blends with acetyl cellulose.⁵ The permeability characteristics of such polymeric alloys are quite different from those of pure acetyl cellulose.⁶ Poly(vinylpyrrolidone) (PVP) becomes insoluble in water after it is mixed with "in situ" formed polyurethanes, and the thus obtained material acts as an efficient hyperfiltration membrane.⁴ We noted that PVP tends also to form polymeric alloys with various aromatic polyamides.⁷

The synthesis of a high molecular weight macrocyclic polyether-polyamide and properties of its blends with PVP are described in the present paper.

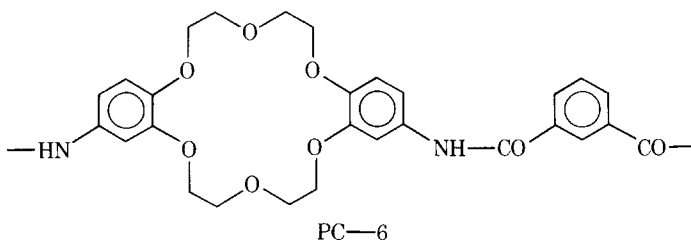
Permeability characteristics of membranes prepared from these materials were described elsewhere.⁸

EXPERIMENTAL

Poly(vinylpyrrolidone) (PVP). GAF Corp. U.S.A., MW = 360,000, was dried under vacuum (10^{-6} torr) at room temperature for 24 hr.

cis-4,4'-Diamino-dibenzo-18-crown-6 (AmDBC), mp 178–9°C, was prepared as described elsewhere.⁹ Its pmr spectrum taken in deuterated pyridine shows the H(6) doublet at 6.88 ppm ($J = 8.5$ Hz) and the H(3;5) and CH₂—O multiplets at 6.49 ppm and 3.98 ppm, respectively.

The Macrocyclic Polyether-Polyamide (PC-6). It was synthesized by polycondensation of AmDBC with isophthaloyl chloride (ICL), Fluka, purum:



8.278 g ICL was distilled under vacuum into a 250-ml reaction flask. 15.82 g of AmDBC (99.3% of stoichiometric amount) was dissolved under dry argon in 200 ml dry hexamethylphosphoramide (HMPA), and the solution was added to the reaction flask. The reaction mixture was slowly stirred with a magnetic stirrer. It was kept under argon atmosphere and was cooled with ice water. After 30 min, all ICL crystals disappeared and the cooling was discontinued. After another hr, the solution became extremely viscous. It was diluted with N-methylpyrrolidone. The polymer was precipitated by pouring the solution into vigorously stirred methanol. The product was filtered, placed in a Soxhlet, and the residual solvents were extracted with acetone. Its intrinsic viscosity in HMPA at 30° is $7.5 \text{ g}^{-1} \text{ dl}$.

HMPA. It was purified by drying on molecular sieves type 4A. Traces of dimethylamine were removed under vacuum (24 hr at 10^{-6} torr). Thus, purified HMPA was distilled and the middle fraction (60–63°/0.3 torr) was collected. It was stored under argon over molecular sieves 4A.

Preparation of Polymeric Alloys. The dried polymer and its mixtures with PVP were dissolved in DMF containing NaSCN (1:1 ratio between salt and macrocyclic rings). The polymer solutions were in the concentration range of 3–7%. Millipore XX3001200 swinny filter holder attached to a 20-ml syringe was used for filtering the solutions from any traces of insoluble impurities; 25 to 50 μ -thick films were cast on glass plates cleaned, prior to use, with 3% HF solution. The solvent was slowly evaporated at room temperature at 0.5 torr. Films were removed from the glass plates after 24 hr and further dried under vacuum (10^{-6} torr, 90°) for 72 hr.

Films were also cast from hexafluoroisopropanol (HFP) solutions. Traces of HFP which remained in such films after 24 hr at room temperature were removed under vacuum of 20 torr.

Mechanical Properties of Films. These were determined according to ASTM D-882-61T with an Instron Universal Testing Instrument Model 1114. Stripes of films, 100 mm long and 8 mm wide, were used. The separation between grips was 50 mm, and the rate of grip separation was 5 mm/min.

Thermal Characteristics. Thermal characteristics of the films were determined with a Perkin-Elmer instrument. The penetration unit TMS-1 and the differential scanning calorimeter DSC 1B were used for the determinations of the transition temperatures. Thermal stability was measured with DSC 1B and with the thermogravimetric analyser TGS-1.

Rate of Extraction. The rate of extraction of PVP from the polymeric alloys was determined using the following analytical procedure: films were stirred with measured amounts of distilled water. The concentration of PVP in the aqueous solutions were determined colorimetrically¹⁰; 2 ml acetic acid and 5 ml iodine reagent ($2.5 \times 10^{-3} M I_2 + 1.3 \times 10^{-2} M KI$ in 2.5% aqueous $ZnSO_4$) were added to 8-ml aliquots of tested solutions. The absorbance of these solutions was measured at 432 nm against a blanc solution. This method enabled us to detect PVP in the concentration range of 0.5–80 ppm. No interference due to the presence of $10^{-2} M NaSCN$ and 0.25% DMF was noted.

Scanning Electron Micrographs. These were taken on the dried alloy membranes at magnifications of 1,000 to 30,000. Some of the samples were equilibrated in 1 M $Pb(NO_3)_2$ solutions prior to drying, or cast from $Pb(NO_3)_2$ solution in N-methylpyrrolidone ($\frac{1}{2}$ equivalent of Pb ions per "crown" ether). Such labeling of the "crown" ethers with the heavy metal ions did not reveal any heterogeneity in the films.

RESULTS AND DISCUSSION

A macrocyclic polyether-polyamide chemically identical with PC-6, but of a lower molecular weight ($[\eta] = 0.6\text{--}1.0 g^{-1} dl$) was first synthesized by Feigenbaum and Michel.¹¹ In our laboratory, polymers in the same viscosity range ($[\eta] = 0.7\text{--}0.8 g^{-1} dl$) were also obtained by their procedure. However, the mechanical properties of membranes prepared from these polymers were unsatisfactory. Upon wetting, they become brittle and cracked easily. On the other hand, the high molecular weight PC-6 yielded tough films which were not affected adversely by exposure to water and various organic solvents. Their mechanical properties are summarized in Table I. The high and the low molecular weight polyamides differ significantly in their elongation properties. Films prepared from PC-6 were suitable for permeation and hyperfiltration experiments.⁸

The method of preparation of PC-6 represents a modification of the interfacial polycondensation technique in which the reaction takes place near the surface of the dichloride crystals. High molecular weight polymers are obtained in interfacial polycondensations when the diffusing diamine molecule has much higher probability to react with the growing polymer than with a new diacid chloride.¹³ This may be the case in our system. The very high viscosity of PC-6 in HMPA ($[\eta]^{30^\circ} = 7.5$) could, however, also be attributed to branching under conditions which may favor the formation of secondary imide groups (high local concentration of acichloride). To check this possi-

TABLE I
Mechanical Properties of Crown-Polyamide Membranes

Film	Method of preparation ^d	Tensile strength (kg/cm ²)		Modulus of elasticity, kg/cm ²	Elongation, %	
		ultimate	at yield		At yield	At break
PC-6	1	580	585	22700	3.6	135
	2	650	608	23250	4.1	175
	3	525	515	19700	4.2	153
A(20) ^a	2	470	510	22000	3.3	180
	3	535	488	19400	3.7	150
F & M polymer ^b	—	700	—	20000	—	12
Aromatic polyamide ^c	—	640	—	22600	—	—

^a Polymeric alloy. The number in parenthesis designates the weight per cent of PVP in the dry alloy.

^b Low molecular weight macrocyclic polyether-polyamide. Values taken from ref. 11.

^c Chemstrand aromatic polyamide used for reverse osmosis. Values taken from ref. 12.

^d 1 = Membranes cast from HFP; 2 = cast from DMF + NaSCN and rinsed with water for 24 hrs; 3 = cast as 2 and rinsed with 1 M NaSCN.

bility, an attempt was made to determine viscosities in 96% H₂SO₄. (It was shown, in the case of aliphatic polyamides, that a selective hydrolysis of the imide branching links take place in this solvent.^{14,15}) Such determinations yielded $[\eta]_{\text{H}_2\text{SO}_4}^{30^\circ} = 0.5 \text{ g}^{-1} \text{ dl}$ for the polymer prepared according to procedure of reference 11, and $[\eta]_{\text{H}_2\text{SO}_4}^{30^\circ} = 2.7 \text{ g}^{-1} \text{ dl}$ for PC-6.

Examination of samples recovered after viscosity determinations from the sulfuric acid solutions revealed, however, that the polymers were converted into their sulfonic acid derivatives. Apparently, the two etheral groups in the ring make it extremely susceptible to electrophilic attack. Thus obtained ionically charged polyamides are water soluble. They are presently under detailed investigation, and their properties will be reported at a later date.

Obviously, the sulfuric acid test which was designed to detect branching due to the presence of the imide links cannot be used in our system. The possibility that some branching occurs during the formation of PC-6 cannot, therefore, be ruled out at the present time. Nevertheless, the viscosity results in sulfuric acid solutions clearly indicate that the sulfonated PC-6, which is certainly free from the imide side groups, has also a very high molecular weight.

Polymeric blends of PC-6 with PVP which contain up to 30% PVP have been cast from DMF solutions (see experimental section). Transparent, mechanically strong films are thus obtained. The added PVP does not change significantly the mechanical properties of PC-6 (Table I) but causes a considerable increase in the hygroscopicity of the material.⁸ Scanning electron micrographs of the blends did not reveal any separate microphase regions (see experimental section). An intimate blending of the two components in the membrane is also indicated by the fact that the water-soluble PVP cannot be leached out from it by extraction with water at room temperature. Thus, only 0.1% of the PVP were removed from the A(30) as result of 48 hr of ex-

TABLE II
Transition Temperatures of PVP, PC-6, and Their A(30) Alloy

Method of Determination	PVP	A(30) ^a		PC-6	
		Free of ions	Equilibrated with 1M NaSCN ^b	Free of ions	Equilibrated with 1M NaSCN ^c
T'' , °C Penetration	—	32–36 ^d	42–45 ^e	42–50 ^f	—
T' , °C Penetration	168	214–216	225	214–217	247
DSC	177	206		210	

^a The number in parenthesis designates the weight per cent of PVP in the dry alloy.

^b The concentration of NaSCN in the alloy is 1.16 mmole/cc.

^c The concentration of NaSCN in the polymer is 1.92 mmole/cc.

^{d,e,f} Water-saturated samples, volume fractions of water are 0.325, 0.25, and 0.20, respectively.

traction at R.T., and the extracted amount decreased to 0.04% when the extraction was continued for additional 720 hr. Probably, traces of PVP which were initially extracted came from the surface of the membranes or belonged to the low molecular weight "tail" of the PVP. The A(20) membranes retained more than 99.8% of their PVP content after 70 days of extraction at room temperature.

The high affinity of PVP toward PC-6 was also demonstrated by the following experiment: DMF solution of the polymeric mixture was poured into vigorously stirred water. Under these conditions, 89% of the PVP were retained by the finely dispersed precipitate.

A useful information about the homogeneity of blends is also provided by the comparison of their transition temperatures with those of their parent polymers.² In microphase-separated blends, the individual transitions of the components are detectable, while in homogeneous mixtures, new transitions appear which correspond to weighted averages of those of the components.^{2,5} Transition temperatures, which were determined by the penetration technique and by the differential scanning calorimetry (DSC), are summarized in

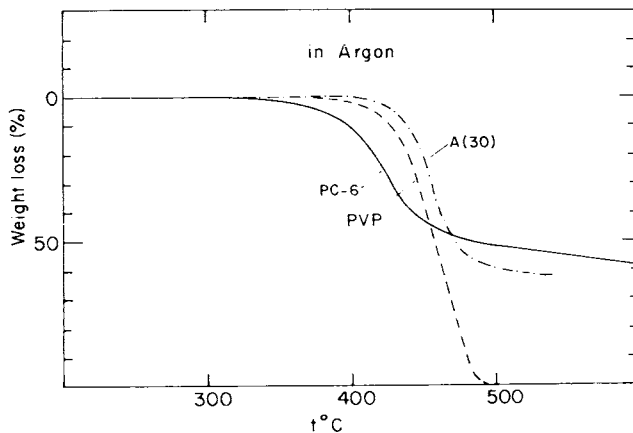


Fig. 1. Thermogravimetric analysis of PC-6, PVP, and of their polymeric alloy (30% PVP). Argon atmosphere; rate of heating, 16°C/min.

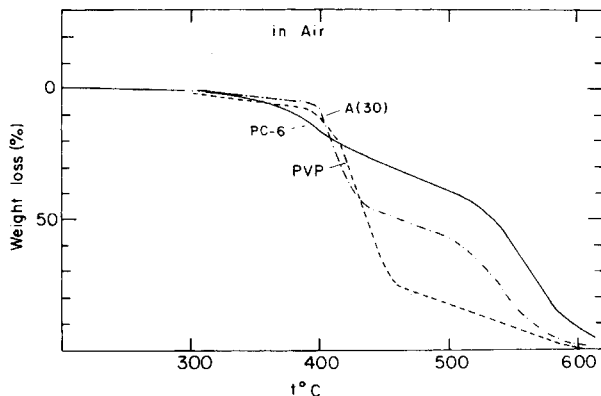


Fig. 2. Thermogravimetric analysis of PC-6, PVP, and of their polymeric alloy (30% PVP). Rate of heating in air, 8°C/min.

Table II. The two methods yielded values which did not differ by more than 10°C. In all dry samples only a single transition was detected. However, a second transition (T'') could also be noted in water-saturated samples. At transitions denoted as T' , the penetration of the samples by the penetrometer needle was total. Hence, T' may be considered to be T_m rather than T_g . It may be seen from the tabulated results that no separate transition which could be attributed to the PVP regions appears in the alloy membranes.

The values of T' seem to be considerably affected by the presence of the complexed salts in the membranes. In such case, T' of the alloy is approximately equal to the weighted average of the components. However, T' of pure A(30) is essentially identical with that of pure PC-6. The similarity of T' of pure PC-6 and A(30) seem to indicate that the polyamide-polyamide interactions are partially replaced in the blend by equally strong polyamide-PVP interactions.

An interesting effect of PVP on PC-6 is noted when the DSC measurements are extended to higher temperatures. Namely, the strong exothermic peak which appears in pure PC-6 at 275° is shifted by 75°C in the presence of PVP, i.e., it appears in A(30) at about 350°C. An even more striking evidence for the stabilizing effect due to the PVP-PC-6 interactions is provided by thermogravimetric analysis. It may be seen from Figure 1 that in inert atmosphere the evolution of volatile products starts in the case of A(30) only at 410°C, hence at temperature ~30° higher than for PVP and 70°C higher than for pure PC-6. The stabilizing effect of PVP is less pronounced in air (cf. Fig. 2). However, also under such conditions the decomposition starts only above 400°C. Inspection of samples heated for 5 min at 250°C (under nitrogen) again provides evidence of the stabilizing effect due to the presence of PVP. PC-6, under such conditions, undergoes crosslinking and becomes insoluble in DMF-NaSCN solutions, while the solubility characteristics of A(30) do not seem to be affected by such treatment.

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