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Chelate membrane from poly(vinyl alcohol)/poly(*N*-salicylidene allyl amine) blend. I: Synthesis and characterization of Co(II) chelate membrane

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A Co(II) chelate membrane from a poly(vinyl alcohol)/poly(allyl amine) blend was synthesized. As an intermediate step the blend membrane was modified to a Schiff-base type. Structures of blend and Schiff-base membrane were confirmed by the *FT*i.r. subtraction method. Differential scanning calorimetry thermograms of blend and Schiff-base membranes showed that the glass transition temperature (T_g) ranges between 40 and 50°C. Co(II) content in chelate membrane was determined by electron dispersive X-ray spectroscopy, elemental analysis and thermogravimetric analysis and ranged between 9.82 and 15.75 wt%. As the membrane becomes chelate with Co(II), the density increases as measured by a density gradient column.

(Keywords: chelate membrane; PVA/poly(allyl amine) blend; Schiff base)

INTRODUCTION

Polymeric chelate membranes for facilitated gas transport can be prepared by two methods, blending the chelate portion with a polymer and grafting the chelate portion on to the side chain of the polymer[1–3]. In the former case, about 30 wt% metal content in the material has been reported[4]. However, for a graft polymer less than 10 wt% metal content was achieved because of the brittleness of the membrane[5].

Poly(ally amine) (PAAm) possesses an amino group in the side chain that is highly reactive and oxidizes in air. There are several reports on the application of PAAm[6–7]. Poly(vinyl alcohol) (PVA) is a hydrophilic polymer and has hydroxyl groups which are known to be weakly acidic.

Compatibilization of the blend polymer can be characterized by optical methods such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM)[8,9] and thermal analysis[10]. Some workers confirmed the characteristic peaks of the blend under the assumption that if there existed an interaction between two polymers in the polystyrene/poly(vinyl methyl ether) blend, there should be a characteristic interaction peak on comparing their Fourier transform infra-red (*FT*i.r.) spectra[11–13]. Wöhrle *et al.* synthesized and characterized polymeric Schiff base/Co(II) chelates from 2-hydroxy-5-vinylbenzaldehyde and 4,4'-divinylsalen, and studied their dioxygen binding and catalytic activity[14–16]. According to their study, covalently bound polymer chelates show high activity for the reversible binding of dioxygen under the formation of mononuclear superoxo complexes.

In the present study, it is our objective to prepare higher metal-containing PAAm/PVA blend chelate membranes for future use in gas separation and to investigate their blend characteristics. To incorporate Co(II) in the membrane, PAAm was converted to the Schiff base by reacting it with salicylaldehyde to make a stable ligand. The structural changes and the properties at each reaction step were investigated using differential scanning calorimetry (d.s.c.), electron dispersive X-ray spectrometry (EDX), X-rays, elemental analysis (EA) and density measurements.

EXPERIMENTAL

Reagents and instruments

Poly(vinyl alcohol) (PVA, M_w 66000, degree of hydrolysis 88%) and poly(allyl amine hydrochloride (PAAm.HCl) were purchased from Shinyo Chemicals and Aldrich Chemicals, respectively. Diaion SA 10A, a strong anion exchange resin, was purchased from Samyang Co., Ltd. Salicylaldehyde and Co(acetate)$_2$.6H$_2$O were reagent grade from Junsei Chemical Co.

To identify the structure of blend and the materials at each modification step, *FT*i.r. (Nicolet Model Magna IR 550) was used. EA (Carlo Erba Elemental Analyser Model 1108) was used to measure the content of Co(II) in chelate membranes, and X-ray (Rigaku Denki Model RAD-C) to study the structure of synthesized membranes. Thermal properties were studied by differential scanning

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calorimetry (d.s.c.) (Du Pont Model 910, −30 to 300°C, 10°C min^{-1}).

Blend of PVA/PAAm

PAAm.HCl was dissolved in deionized water (10 wt%), 200 vol% anion exchange resin was added and filtered with a glass filter. The resin was dried in a freezing drier. PVA and the obtained PAAm were dissolved separately in deionized water (5 wt%), and blended in a weight ratio of PVA:PAAm of 3, 4, 5 and 6. The membranes were cast on an acrylic plate and dried in a vacuum oven at 40°C for 2 days to obtain transparent membranes (Ble) of 30–50 μm thickness.

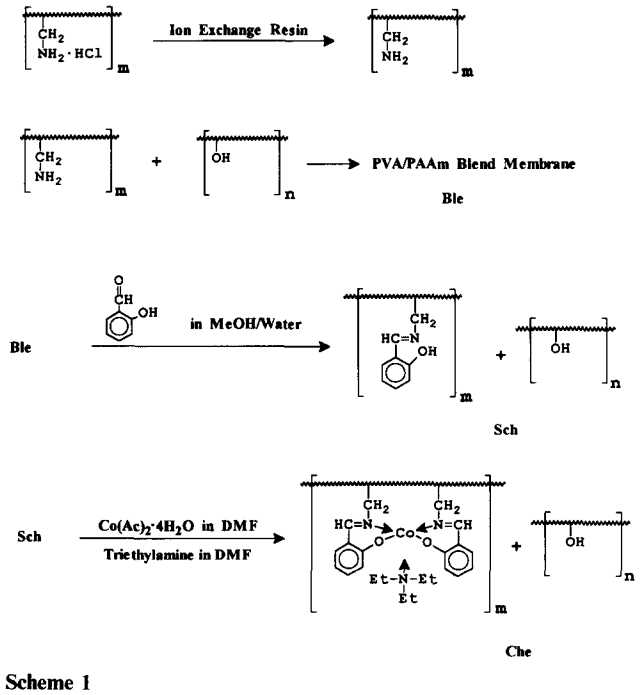
Schiff-base membranes

The blend membrane was dipped in a salicyaldehyde solution where salicylaldehyde:deionized water:methanol = 1:1:4 (vol. ratio) for 30 min followed by washing in methanol and deionized water mixture. The obtained yellowish membrane (Sch) was dried in a vacuum oven at 40°C for 1 day.

Co(II) chelate membranes

Schiff-base membrane was swollen in DMF at 60°C followed by adding Co(acetate)$_2$.6H$_2$O and triethylamine (TEA) for 14 h. The membrane was washed with methanol containing excessive TEA, then dried in a vacuum oven. Since the transition metal contained in the polymer can be oxidized easily, TEA was introduced as an axial ligand. The oxidation of the transition metal may affect the capacity to adsorb oxygen[17]. Immediately after the chelation, the chelate membrane (Che) was stored in a nitrogen environment.

The synthetic scheme is shown in *Scheme 1*. The sample designations are listed in *Table 1*.



Scheme 1

RESULTS AND DISCUSSION

FT-*i.r. and EDX*

Figure 1 illustrates the *FT*i.r. spectra of (a) Ble 3:1, (b) PVA, (c) PAAm and (d) the subtraction peak of each pure component from the blend. We can see that the peak that appeared at 1600 cm^{-1} was identified to be $-NH_3^+$, which was formed between the hydroxyl group in PVA and the amino group in PAAm. Ble 3:1 was further treated with salicylaldehyde to make Sch 3:1 (see *Figure 2b*) and later soaked in Co(II) solution to prepare Che 3:1 (see *Figure 2c*). $\nu_{C=N}$ appeared at 1650 cm^{-1}, ν_{OH} in aromatic ring at 1270 cm^{-1} and *ortho*-substituted aromatic peaks were seen at 770–730 cm^{-1} as Ble 3:1 becomes Sch 3:1. It was expected that the hydroxyl group in PVA can also react with aldehyde. When PVA was treated with salicylaldehyde under the same conditions

Table 1 Designation and cobalt contents of membranes

	Initial weight ratio of PVA/PAAm	Density (g cm^{-3})[a]	Co(II) content (wt%)[b]
Ble 3:1	3		–
Ble 4:1	4		–
Ble 5:1	5		–
Ble 6:1	6		–
Sch 3:1	3	1.22	–
Sch 4:1	4	1.23	–
Sch 5:1	5	1.24	–
Sch 6:1	6	1.24	–
Che 3:1	3	1.36	15.75
Che 4:1	4	1.36	12.48
Che 5:1	5	1.37	11.28
Che 6:1	6	1.39	9.82

[a] Density of PVA: 1.26 g cm^{-3}
[b] Determined by EA

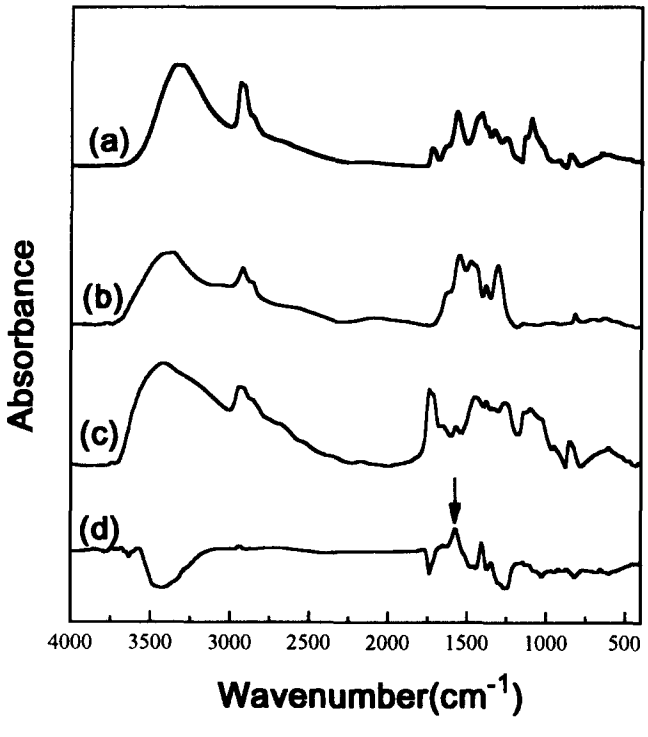


Figure 1 *FT*i.r. spectra of (a) Ble 3:1; (b) PVA; (c) PAAm; (d) the subtraction peak of Ble 3:1 from PVA and PAAm

to prepare poly(salicylidene allyl amine), it was confirmed that no distinctive difference was seen in *FT*i.r. spectra. Therefore, the Schiff base is formed mainly in the PAAm portion. After the Schiff-base sample was treated with Co(II) solution, the peak at 1270 cm^{-1} due to –OH in the aromatic ring disappeared, meaning that Co(II) formed a chelate primarily with –OH in the salicylidene group.

Detection of the incorporation of Co(II) by *FT*i.r. spectra of samples was not successful. In the EDX spectra shown in *Figure 3*, the peak intensity of Co(II) decreases as the PVA content increases.

Elemental analysis (EA)

Co(II) content was determined by EA (*Table 2*). Values range between 9.82 and 15.75 wt%. Observed Co(II) content is greater than the theoretical value. This result suggests that Co(II) is introduced to some extent to the –OH group of PVA[18].

According to the study of Wöhrle *et al.*, excessive cobalt in the polymer compared with the calculated Co(II) content (ca. 7 wt% in our study) did not influence the reversible oxygen uptake. In this case, only Schiff base ligand-bound cobalt is active[16].

Thermal properties

Thermal properties of the blend and chelate membranes were characterized using d.s.c. (*Figures 4–7*). In *Figure 4*, glass transition temperature (T_g) and crystalline melting temperature (T_m) of PVA (curve b) appeared at 65 and 190°C, respectively, while T_g of PAAm (curve a) appeared at 28°C and no T_m of PAAm was observed. T_g of the Ble 3:1 (curve c) appeared at 42°C between the T_gs of the two components. T_g of Sch 3:1 membrane (curve d) was shown at 39°C. However, T_g of the chelate membrane (Che 3:1) (curve e) was not observed. There appears a broad endothermic peak at around 120–190°C in the blend sample, attributed to the melting of PVA and that of ionic clusters formed between the amino group in PAAm and the hydroxyl group in PVA. When the crystalline polymer copolymerizes with ionomer, there appears a melting peak due to the formation of ionic

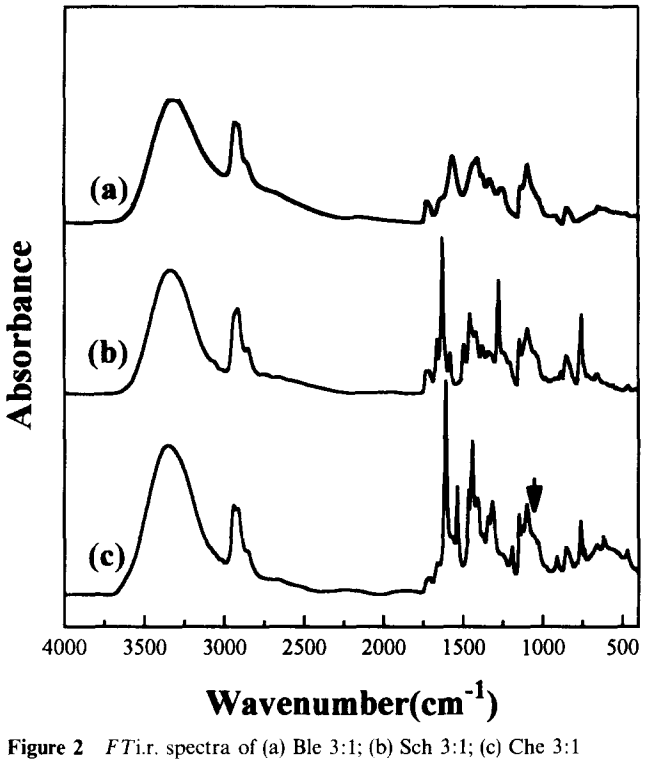


Figure 2 *FT*i.r. spectra of (a) Ble 3:1; (b) Sch 3:1; (c) Che 3:1

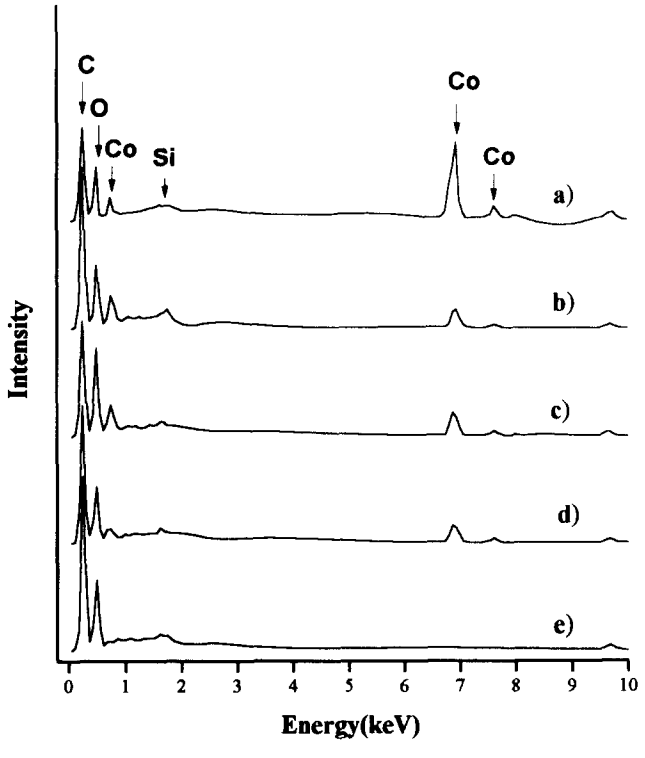


Figure 3 EDX spectra of (a) Che 3:1; (b) Che 4:1; (c) Che 5:1; (d) Che 6:1; (e) Sch 3:1

Table 2 EA results for Sch and Che membranes

	C		H		O		N		Co(II) content	
Sample	Calc.	Found	Calc.	Found	Calc.	Found	Calc	Found	Calc.[a]	Found
Sch 3:1	64.80	63.32	7.99	9.09	23.12	22.33	4.09	4.11		
Sch 4:1	63.15	61.82	8.04	9.44	25.16	24.05	3.65	3.72		
Sch 5:1	62.11	54.62	8.16	9.94	26.55	28.48	3.18	3.25		
Sch 6:1	61.31	52.95	8.25	10.02	27.62	28.66	2.82	2.67		
Che 3:1	61.06	49.52	8.26	7.01	18.75	23.05	4.96	5.34	11.03	15.75
Che 4:1	60.02	50.59	8.72	7.02	20.82	27.22	4.53	1.59	6.44	12.48
Che 5:1	59.49	49.47	8.35	8.02	22.46	27.11	4.04	2.71	5.43	11.28
Che 6:1	59.47	45.02	8.32	7.25	23.54	28.92	3.61	2.48	5.22	9.82

[a] Calculated from nitrogen content

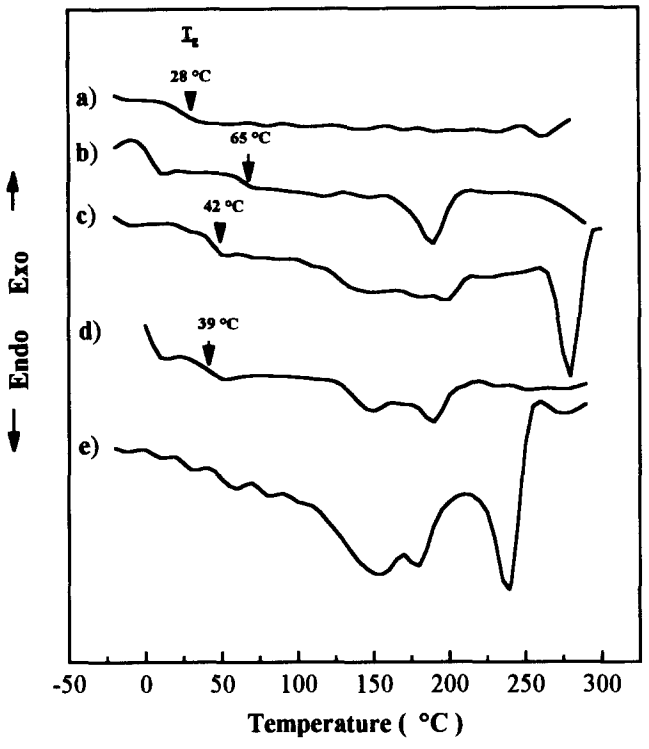


Figure 4 D.s.c. thermograms of (a) PAAm; (b) PVA; (c) Ble 3:1; (d) Sch 3:1; (e) Che 3:1

clusters or ionic crystals prior to the melting of crystalline polymers[19]. We observed similar results to those of Hirasawa[19]. As can be seen in *Figure 4*, the melting endotherm, which appeared at 120–190°C, of Schiff-base membrane was distinguished from that of PVA and became larger. This means that hydrogen bonding between Schiff base and hydroxyl groups in PVA and salicylidene group is stronger than electrostatic interaction between amino group and hydroxyl group in blend membranes. In a chelate membrane, the melting peak of the ionic cluster is larger than that of Schiff base, because the interaction of ionic cluster becomes stronger as the membrane becomes a chelate with Co(II).

Figure 5 illustrates the d.s.c. thermograms of PAAm (curve a), blends (curves b–e) and PVA (curve f). The T_gs of the blends are between the T_gs of PAAm and PVA, except for Ble 5:1 which has a large ionic cluster peak shown at around 130–220°C.

Figure 6 represents the thermograms of Schiff-base membranes. The T_g of poly(salicylidene allyl amine) itself was seen at 65°C and was similar to that of PVA. However, T_gs of Sch membranes were in the range 39–48°C, which were below the T_gs of the two polymers. A possible reason might be that in the process of making Sch membranes, the blend membrane formed on the acrylic plate was swollen in 80 wt% methanol solution, and then soaked in salicylaldehyde to form Schiff base and dried at 40°C for 1 day. Therefore, the polymer chain in the membrane was in a restricted state during and after the reaction. Sch membranes were less dense than PVA or poly(salicylidene allyl amine), as shown in *Figure 8*. This artifact may affect the decrease of T_g of Sch membranes. If we had blended the PVA and poly(salicylidene allyl amine) in a solution form, then the T_g of this type would have been at around 65°C. Unfortunately, we could not confirm the T_g of this type, because we could not find the right solvent mixture to prepare the blend.

As shown in *Figure 4*, T_g of Che membrane is not observed, and it is the same with all Che samples. Belfiore *et al.*[20] reported on the synergistic thermal properties of polymeric coordination complexes based on transition metals. According to their study, in the polymeric coordination complexes, T_g increased with metal content to some extent. However, it disappeared at a certain metal

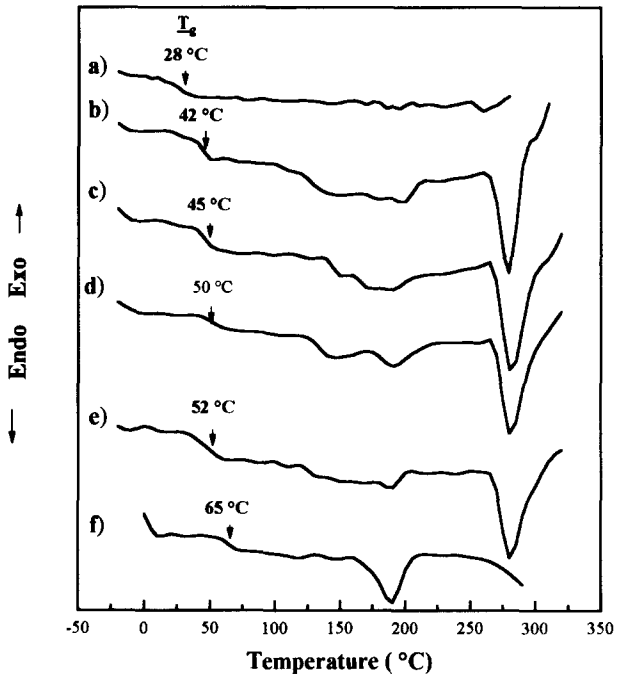


Figure 5 D.s.c. thermograms of (a) PAAm; (b) Ble 3:1; (c) Ble 4:1; (d) Ble 5:1; (e) 6:1; (f) PVA

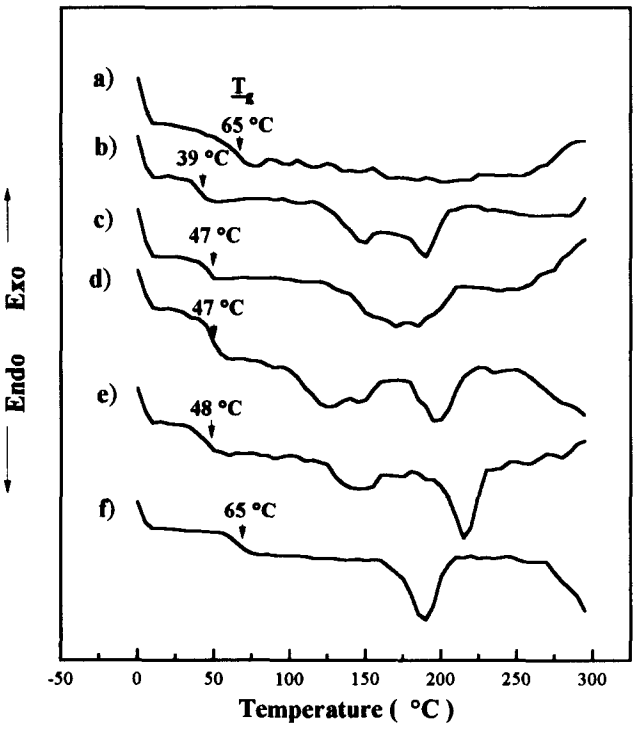


Figure 6 D.s.c. thermograms of (a) poly(salycilidene allylamine); (b) Sch 3:1; (c) Sch 4:1; (d) Sch 5:1; (e) Sch 6:1; (f) PVA

content because of the synergistic effect, described from an energetic viewpoint by focusing on the electron energy of the metal d-electrons and the subsequent ligand field stabilization for complexes, and coordination crosslinks where the mobility of the polymer chain is severely restricted. In our study, chelates in which the covalent bond and coordination bond coexist show similar results.

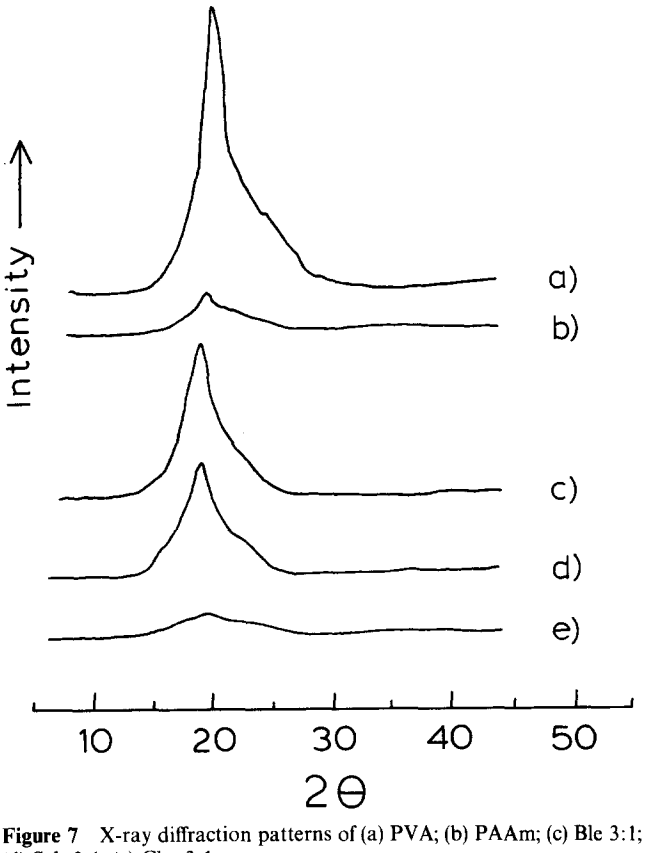


Figure 7 X-ray diffraction patterns of (a) PVA; (b) PAAm; (c) Ble 3:1; (d) Sch 3:1; (e) Che 3:1

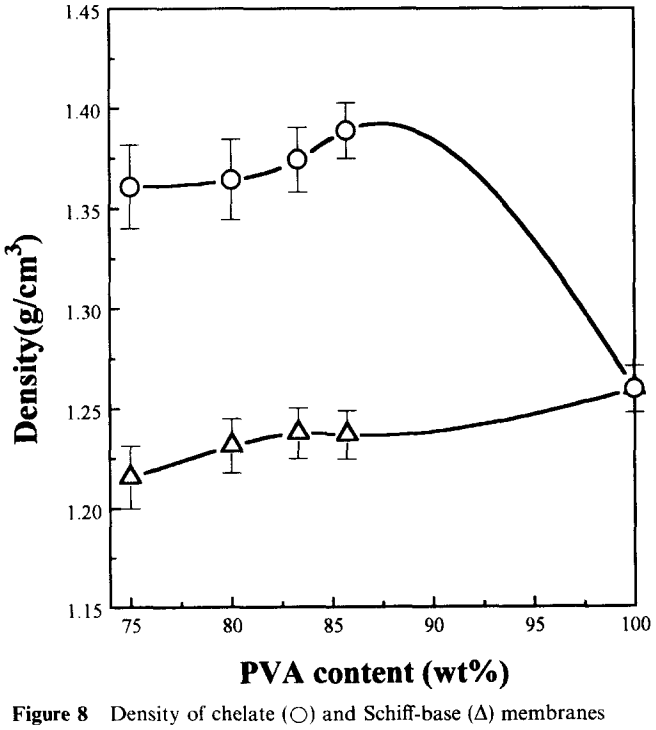


Figure 8 Density of chelate (○) and Schiff-base (Δ) membranes

X-ray diffraction patterns and density

Since the gas permeability was generally influenced by the intersegmental motion, free volume, crystallinity and density, we observed X-ray diffraction patterns (*Figure 7*) and density of samples (*Figure 8*). The crystalline peak measured at $2\theta = 20°$ due to the (101), (200) plane of PVA crystal[21] was reduced as the blend (curve b) was becoming Schiff-base (curve c) and chelate membrane (curve d). Amorphous PAAm contributed to the reduced crystalline peak of the blend. The bulky salicylidene group in Schiff base may break the dense structure to some extent in the PVA/PAAm acid–base complex. Also, the chelate membrane becomes amorphous due primarily to the crosslinked structure between Co(II) and two salicylidene groups in the Schiff-base material.

Figure 8 represents the density changes in various materials. In the density gradient column, n-heptane and carbon tetrachloride and PET were used as a cosolvent and a reference material, respectively. The chelate membrane is denser than the Schiff-base membrane due to the incorporation of the heavy cobalt ion in the polymer chain. In the chelate membrane, the density increases with PVA content and inversely with Co(II) content in the membrane. This can be explained because one Co(II) bonds with two salicylidene groups and upon drying the sample, the free volume of the Che membrane increases with Co(II) content.

CONCLUSIONS

PVA and PAAm blends are compatible in the 3:1–6:1 blending range, contributing to the formation of an acid–base complex between $-NH_2$ in PAAm and –OH in PVA. It was possible to incorporate up to 15.75 wt% Co(II) in a 3:1 blend. Membranes containing above 16 wt% Co(II) become too brittle to be utilized as a membrane. Glass transition temperatures of blend membranes were in the range 42–52°C. The T_g of the Schiff-base membrane appeared at 39–48°C, while the chelate membranes did not show a glass transition. For all the blend and Schiff-base membranes there appear distinctive ionic cluster melting peaks at 130–170°C prior to the crystalline melting peak of PVA at 190°C. During the process of becoming a chelate membrane, the Schiff-base membrane is an effective intermediate step for the preparation of a cobalt-containing chelate membrane. The membrane becomes more amorphous in the process of chelation, as evidenced by X-ray diffraction patterns.

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