Polyetherurethaneurea reinforced poly(vinyl alcohol) dialysis membranes: studies on permeability and mechanical strength

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Abstract. Poly(vinyl alcohol) is a hydrogel which is extensively studied for a variety of biomedical applications. Membranes developed from crosslinked poly(vinyl alcohol) (PVA) is having excellent permeability to solutes. However its wet breaking strength is low. Polyetherurethaneurea (PEUU), having an excellent mechanical strength is blended with PVA as a reinforcement, and membranes developed are studied for its permeability and mechanical strength. The optimum membrane selected, is having permeability and wet breaking strength almost equal to the commercially available cellulose acetate membrane.

Keywords. Haemodialysis membrane; permeability; poly(vinyl alcohol); mechanical strength.

1. Introduction

The vital part of the extracorporeal haemodialyser is the semipermeable membrane that removes certain toxic substances from blood by diffusion. Haemodialysis membranes should have high permeability to solutes, should be blood compatible and should be able to withstand the maximum transmembrane pressure (DHEW 1977). Regenerated cellulosic membranes are currently being used on the largest scale in haemodialysis (Hudson and Cuculo 1980; Ikada 1991) because of its good mechanical strength and solute permeability. Since permeability is directly related to the molecular weight of the solutes, there is little selectivity in the filtering of closely related molecules through cellulosic membranes (Lyman 1964; Hudson and Cuculo 1980), and is known to activate complement system (Ikada 1991). Hence novel membranes need to be developed with good selectivity and mechanical strength.

Poly(vinyl alcohol) (PVA) is used as a basic material for a variety of biomedical applications including contact lens material (Peppas and Yang 1980; Yang *et al* 1981), skin replacement material (Hogemann *et al* 1961; Charadack *et al* 1962), reconstruction of vocal cords (Peppas and Benner 1979, 1980), articular cartilage replacement (Peppas 1979) etc. But its main disadvantage is its weak mechanical strength (Peppas and Merrill 1977). Partial crystallization by annealing can increase the mechanical strength by 100 fold (Peppas and Merrill 1976). Efforts are also being made to use PVA membranes for artificial kidney applications (Merrill *et al* 1972; Peppas 1977; Aleyamma and Sharma 1988), but its commercial application is limited due to lack of adequate wet breaking strength. With proper composition of hydrophilic and hydrophobic regions, membranes with ample strength and

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permeability can be developed. Many studies have been carried out in this direction (Yamashita *et al* 1979; Ohtsuka *et al* 1980).

We have attempted to develop membranes based on PVA having wet-breaking strength comparable with cellulose acetate membrane. Membranes are prepared from crosslinked PVA by blending PEUU as a reinforcement material in various ratios. Its mechanical and permeability properties are studied.

2. Materials and methods

Polyetherurethaneurea (PEUU 1000) was synthesized by solution polymerization in our laboratory as described elsewhere (Shibatani *et al* 1977). Poly(vinyl alcohol), (MW = 125000, 88% mole hydrolized) was from Polysciences Inc. Standard cellulose acetate membrane (0.1 mm thickness) from Thomas Scientific, Swedesboro, USA was used as control. All chemicals used were of AR grade.

2.1 Preparation of membranes

PVA solution (10g% W/V) prepared in dimethyl sulphoxide, and paraformaldehyde was mixed in the ratio 1 : 1 (w/w) and heated to 60°C. To this 0, 2.8, 4.4 and 6.25 ml of PEUU (20g% W/V) was added and mixed well for 30 min, to obtain blends of different ratios. The solution was kept for sometime to get rid of airbubbles, and spread over a glass plate and heated in an oven at 60°C for 48 h. Membranes were peeled off from glass plate, soaked in con.NaOH solution for 1 h, washed in distilled water and kept overnight in DW. These membranes were of 0.1 mm thickness.

2.2 Octane contact angle

Here the octane/water method was selected as a probe for investigating the polar interactions across polymer/water interface (Hamilton 1972). Contact angle was measured using a goniometer (Kernco Instruments Inc., Texas, USA) as described by Chandy and Sharma (1987). At least 30 angles were measured on each surface, averaged and expressed with standard deviations.

2.3 Degree of hydration

Samples cut in the shape of a disc of equal area were weighed and dipped in DW to attain equilibrium swelling. Samples were taken out of water, blotted with filter paper and the weights determined. The degree of hydration was calculated as

$$QW(\%) = (X_2 - X_1)/X_1 \times 100.$$

where X_1 is the weight of dried samples and X_2 the weight of swollen samples.

2.4 Mechanical strength evaluation

Tensile strength and elongation at break were measured according to the method

of ASTM-D 882 using Universal test machine (Chatillon UTSE-2) at a cross head speed of 2.54 cm/min, at room temperature. For wet strength, dimensions of swollen samples were used for calculation.

2.5 Permeability studies

An equilibrium type dialysis cell (3784-D, Arthur H. Thomas Co. USA) was used for determining the permeability of solutes through the membrane at room temperature.

The membrane was clamped between the two compartments using suitable supporting and sealing device. One compartment was filled with phosphate buffer (pH 7.4) and the other with a mixture of solutes containing urea (100 mg% M.W., 60), creatinine (10 mg%, M.W., 113), uric acid (10 mg%, M.W. 168), inulin (25 mg%, M.W. 5000) and albumin (100 mg%, M.W. 69000) in 0.1 M phosphate buffer, pH 7.4. The permeability of solutes through the membrane for 4 h were analyzed spectrophotometrically employing diacetyl monoxime reagent for urea (Latting 1964), alkaline picric acid for creatinine (Hawk 1965), Folin-Wu method for uric acid (Hawk 1965), phenol-sulphuric acid for inulin (Hodge and Hofreiter 1962) and Folin's reagent for albumin. Permeability percentages were calculated from triplicate experiments.

3. Results and discussion

From the octane contact angle studies (table 1), it seemed that as the concentration of PEUU was increased the membranes became comparatively hydrophobic. Degree of hydration of the membranes also decreased as the PEUU content increased. This may be due to the induced hydrophobic moiety of PEUU which is relatively a hydrophobic polymer. Swelling of hydrogel membranes are mainly due to their amorphous regions (Peppas 1987). Blending makes a decrease in the non-crystalline region which decreases the swelling property of the membranes. Compared to bare PVA membranes the tensile strength of blended membranes (dry and swollen state), increased with the increase in PEUU concentration (table 2). PEUU is a block copolymer containing blocks of low molecular weight polyethers linked together by a urethane group, with an excellent tensile strength and high flexure endurance (Szycher 1991). The wet breaking strength significantly increased when the PEUU content was increased to 20%.

Solute permeability of blended membranes from a mixture of different solutes are given in table 3. Solute permeability is reported as the percentage passed in 4 h as a comparative data. It seems that solute permeability decreased with the PEUU concentration. However it is more than that of cellulose acetate membrane. Even though the blending significantly increased the mechanical properties, the decrease in the degree of hydration had a negative impact on the permeability. It is reported that modifications that increase the strength usually decrease the permeability and methods that improve the permeability degrade the mechanical property (Muir *et al* 1973). Based on the free volume theory of diffusion Yasuda *et al* (1968) indicated that the diffusive permeability of solutes through hydrogel membranes is explained by water content. For PVA films, permeation of water, or water soluble solutes is reported to be dependent on the degree of swelling (Kojima

Table 1. Octane contact angle and degree of hydration of PEUU blended PVA membranes.

Membranes	Percentage of		Octane contact angle (degrees)	Degree of hydration (%)
	PVA	PEUU		
Bare PVA	100	—	135± 4	110
PVA 90/10	90	10	129± 4	105
PVA 85/15	85	15	124± 2	100
PVA 80/20	80	20	118± 3	84
Bare PEUU	—	100	112± 3	11
CA	—	—	130± 3	49

CA, Cellulose acetate.

Table 2. Tensile strength and elongation of PEUU blended PVA membranes.

Membranes	Tensile strength (kg/cm ²)		Elongation (%)	
	Dry	Wet	Dry	Wet
Bare PVA	410± 26	221± 21	255± 16	847± 31
PVA 90/10	431± 26	289± 26	210± 28	794± 16
PVA 85/15	492± 31	305± 23	201± 24	750± 33
PVA 80/20	515± 30	335± 19	194± 33	706± 39
CA	437± 29	394± 11	61± 5	82± 4

Table 3. Permeability of solutes through PEUU blended PVA membranes in 4 h.

Membranes	Permeability (% passed ± S.D)				
	Urea	Creatinine	Uric acid	Inulin	Albumin
Bare PVA	58.9± 2.2	32.2± 1.5	23.5± 1.1	7.3± 0.5	1.5± 0.5
PVA 90/10	56.0± 2.9	26.4± 1.2	21.6± 2.1	6.3± 0.7	1.4± 0.5
PVA 85/15	53.6± 2.6	26.1± 1.2	20.9± 1.1	5.9± 0.6	1.4± 0.6
PVA 80/20	50.1± 2.0	25.5± 1.0	20.9± 2.1	5.9± 0.7	1.3± 0.5
CA	46.2± 1.9	31.5± 1.5	24.3± 0.5	5.8± 0.2	2.9± 0.6

et al 1983). Here also it seems that permeability may be directly proportional to the equilibrium water content.

The membrane with 80/20 blend ratio is selected compromising the mechanical strength and permeability. Further increase in PEUU content, may increase the wet breaking strength, but it will decrease the permeability.

Membranes used for haemodialysis should be highly blood compatible. It is known that cell adhesion is greater on hydrophilic substrates compared to hydrophobic one (Baier 1977), and the adhesion of platelets onto the material surface initiates the thrombus formation (Szycher 1983). Since the blended membranes are comparatively more hydrophobic, cell adhesion onto these surfaces may be less than that of PVA. PVA and PEUU is reported to be highly blood compatible (Ikada *et al* 1981; Szycher 1991). Low clotting tendency of polyurethanes (Boretos

and Pierce 1968) makes them useful in biomedical devices like vascular graft, heart valve, artificial kidney membranes, artificial heart and assist devices (Boretos *et al* 1971; Lyman *et al* 1977). Blood compatible membranes are also being developed (Jayasree and Sharma 1989) from PEUU. However, further studies are required to evaluate the blood compatibility of the blended membranes.

4. Conclusion

From this study it has been shown that the mechanical properties and dialysis performance of PVA membranes are varied by adjusting the blending ratio of PVA and PEUU. Membrane with 80/20 blend ratio is having the highest tensile strength with comparable permeability to cellulose acetate. This membrane showed the possibility of having appropriate mechanical strength and solute permeability suitable for the possible application as dialysis membrane.

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References

- Aleyamma A J and Sharma C P 1988 *Polym. Mater. Sci. Eng. ACS Symp. Ser.* **59** 692
Baier R E 1977 *Ann. N.Y. Acad. Sci.* **283** 17
Boretos J W and Pierce W S 1968 *J. Biomed. Mater. Res.* **2** 121
Boretos J W, Detmer D E and Donachy J H 1971 *J. Biomed. Mater. Res.* **5** 373
Chandy T and Sharma C P 1987 *Polym. Plast. Technol. Eng.* **26** 143
Charadack W M, Brueske D A, Santomauro A P and Fazekas G 1962 *Ann. Surg.* **155** 127
DHEW 1977 Evaluation of haemodialyzers and dialysis membranes, DHEW Pub. No. (NIH) 77-1294, Washington DC
Hamilton W C 1972 *J. Coll. Int. Sci.* **40** 219
Hawk P B 1965 in *Physiological chemistry* (ed.) B L Oser (New York: McGraw Hill) p. 562
Hodge J and Hofreiter L 1962 in *Methods in carbohydrate chemistry* (eds) R L Whistler and M L Wolfrom (New York: Academic Press) Vol. 1, p. 380
Hogemann K E, Gustafson G and Bjorlin G 1961 *Acta Chir. Scand.* **121** 83
Hudson S M and Cuculo L A 1980 *J. Macromol. Sci. Rev. Macromol. Chem.* **18** 1
Ikada Y 1991 *Polym. J.* **23** 551
Ikada Y, Iwata H and Horri F 1981 *J. Biomed. Mater. Res.* **15** 697
Jayasree G and Sharma C P 1989 *J. Biomater. Appl.* **3** 405
Kojima Y, Furuhashi K and Miyasaka K 1983 *J. Appl. Polym. Sci.* **28** 2401
Latting G B 1964 *Am. J. Clin. Path.* **41** 565
Lyman D J 1964 *Trans. Am. Soc. Artif. Int. Org.* **10** 17
Lyman D J, Seare W J, Albo D, Bergman S, Lamb J, Metcalf L C and Richards K 1977 *Int. J. Polym. Mater.* **5** 221
Merrill E W, Salzman E W, Wong D S and Silliman L 1972 *J. Polym. Prep. Am. Chem. Soc. Div. Polym. Chem.* **13** 511
Muir W M, Gray P A, Courtney J M and Ritchie P D 1973 *J. Biomed. Mater. Res.* **7** 3
Ohtsuka Y, Hirabayashi Y and Takayama S 1980 *Kobunshi Ronbunshu* **37** 507
Peppas N A 1977 *Polym. Prep. Am. Chem. Soc. Div. Polym. Chem.* **18** 794
Peppas N A 1979 *Biomater. Med. Dev. Art. Org.* **7** 421
Peppas N A (ed.) 1987 in *Hydrogels in medicine and pharmacy* (Florida: C R C Press Inc.) Vol. II, p. 1

- Peppas N A and Merrill E W 1976 *J. Polym. Sci. Polym. Chem. Ed.* **14** 441
- Peppas N A and Merrill E W 1977 *J. Appl. Polym. Sci.* **21** 1763
- Peppas N A and Benner R E Jr 1979 *Proc. IUPAC* **26** 1539
- Peppas N A and Benner R E Jr 1980 *Biomaterials* **1** 158
- Peppas N A and Yang W H 1980 *Proc. IUPAC* **27** 28
- Shibatani K, Lyman D J, Shiek D F and Knutson K 1977 *J. Polym. Sci. Polym. Chem. Ed.* **15** 1655
- Szycher M (ed.) 1983 in *Bio compatible polymers, metals and composites* (Pennsylvania: Technomic Publ. Co. Inc.) p. 16
- Szycher M 1991 in *Blood compatible materials and devices: Perspectives towards the 21st Century* (eds) C P Sharma and M Szycher (Pennsylvania: Technomic Publ. Co. Inc.) p. 33
- Yamashita S, Nagata S and Takakura K 1979 *Kobunshi Ronbunshu* **36** 249
- Yang W H, Smolen V F and Peppas N A 1981 *J. Membr. Sci.* **9** 53
- Yasuda H, Lamaze C E and Ikenberry L D 1968 *Macromol. Chem.* **118** 19