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39. Permeation Characteristics and Structure of Polymer Blend Membranes from Poly(vinylidene fluoride) and Poly(ethylene glycol)

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Summary

The permeation characteristics of polymer blend membranes from poly(vinylidene fluoride) and poly(ethylene glycol) to aqueous polymer solution were investigated under carefully controlled conditions. The permeation characteristics were influenced significantly by the blend ratio, the temperature and time of heat treatment, which changed the structure of the resulting membranes.

Introduction

It has been well known[1,2] that membranes prepared by adding in the casting solution the additive such as magnesium perchlorate and barium perchlorate give higher permeation rate without lowering rejection for the solute in the feed solution. It is required to control size and number of pores in the membrane in order to make membranes for the separation of polymer solute which have higher permeation rate and rejection. In this paper, poly(ethylene glycol), which can be dissolved out during gelation process in water and heat treatment in hot water, is used as polymer additive to control pore size and pore number of poly(vinylidene fluoride) membranes. Permeation characteristics and structure of the resulting membranes are discussed.

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Experimental

Materials Poly(vinylidene fluoride)(PVF_2)(produced by Kureha Chemical Co. Ltd.), whose average degree of polymerization was 1000, and poly(ethylene glycol)(PEG 20000)(supplied by Sanyo Kasei Co. Ltd.), whose number average molecular weight was 18000-25000, were employed as membrane substance. Pure commercial dimethyl formamide(DMF) and tetrahydrofuran (THF) were used as solvents for the casting solution. Poly(vinyl alcohol)(PVA 205)(supplied by Kurary Co. Ltd.) having 550±50 of average degree of polymerization was used as the solute of feed solution.

Preparation of membranes Poly(vinylidene fluoride)-poly(ethylene glycol) membranes were made by pouring the casting solutions consisting of the proportion poly(vinylidene fluoride)/tetrahydrofuran /dimethyl formamide as 10/40/50 (wt%), containing desired amounts of poly(ethylene glycol) onto a rimmed glass plate, allowing to evaporate the solvent at 25 ^{o}C for 2 h, and immersing the glass plate together with the membranes into a gelation medium (water at 25 ^{o}C). After immersion for 24 h in water, the membranes were removed from the glass plate and treated with hot water at a desired temperature for a desired period.

Apparatus and measurements The apparatus used and the experimental procedure have been described in an earlier paper[2].

Results and Discussion

The effect of additional amount of poly(ethylene glycol) 20000 on the permeation characteristics for aqueous solution of poly(vinyl alcohol) through the polymer blend membranes from poly(vinylidene fluoride) and poly(ethylene glycol) 20000 is shown in Figure 1. The rates of pure water permeability and the permeation rates for aqueous solution of poly(vinyl alcohol)

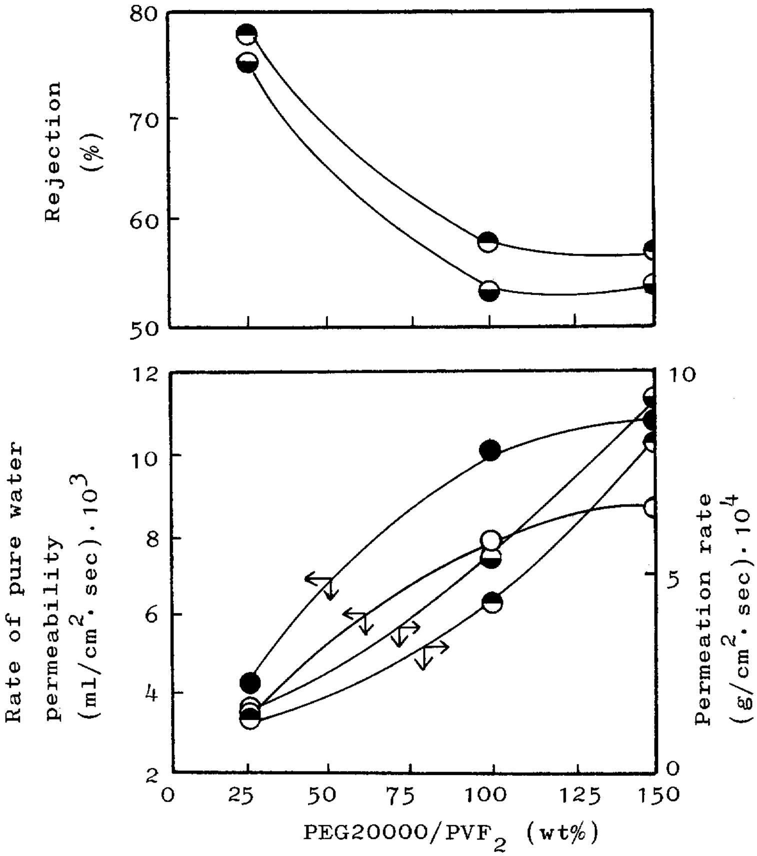


Figure 1. Effect of blend ratio of PEG20000 and PVF_2 on permeation characteristics. Casting solution : PVF_2/THF/DMF=10/40/50 (wt%); membrane preparation: 25 °C, 2 h; (○) pure water, (◓) 1% aqueous solution of PVA 205 for membranes treated in hot water at 60 °C for 20 min; (●) pure water, (◒) 1% aqueous solution of PVA 205 for membranes treated in hot water at 100 °C for 60 min.

205 increase and the rejections for poly(vinyl alcohol) 205 decrease with an increase in additional amount of poly(ethylene glycol). In general, when the polymer concentration in the casting solution is higher, the

decrease of permeation rate and the increase of rejection are given. If one component in the polymer blend is dissolved out during gelation process in water and heat treatment process in hot water, the resulting membranes become rough. Poly(ethylene glycol) is easily dissolved out into water during above processes because it is a very higher water soluble polymer. The increase of permeation rate and the decrease of rejection with the increase in added amount in Figure 1 are attributable to the formation of rough membrane. On the other hand, the membranes prepared at higher temperature of heat treatment in hot water have greater permeation rates and smaller rejections. These results suggest that the amount of poly(ethylene glycol) which is dissolved out from the polymer blend membranes increases with an increase in temperature of heat treatment and greater aggregates of poly(ethylene glycol) molecules in the polymer blend membranes are dissolved out with the temperature of heat treatment.

Figure 2 shows the effect of heat treatment time on the permeation characteristics. The rate of pure water permeability and the permeation rate for aqueous solution of poly(vinyl alcohol) 205 increase remarkably and the rejection for poly(vinyl alcohol) molecules decreases steeply up to 10 min of heat treatment time. In over 10 min the permeation rate decreases and the rejection increases slightly. The formmer phenomenon is attributed to the fact that the poly(ethylene glycol) molecules in the polymer blend membranes are dissolved out into hot water during heat treatment and consequently the membranes having rough structure are formed. The latter phenomenon is dependent on the shrinkage of membrane with heat treatment after the dissolution of poly(ethylene glycol) molecules in the polymer blend membranes.

The scanning electron photomicrographs of the membranes from poly(vinylidene fluoride) and poly-

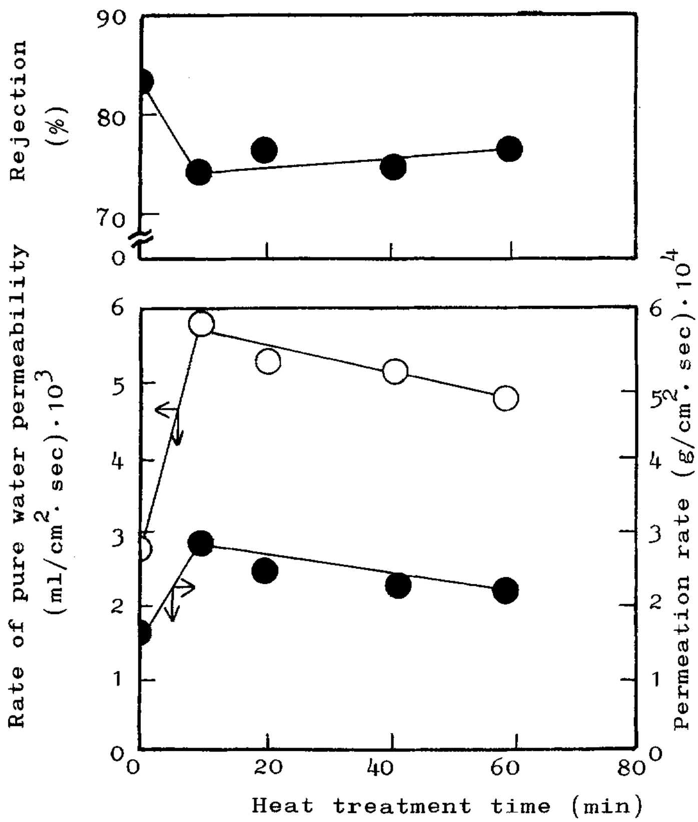
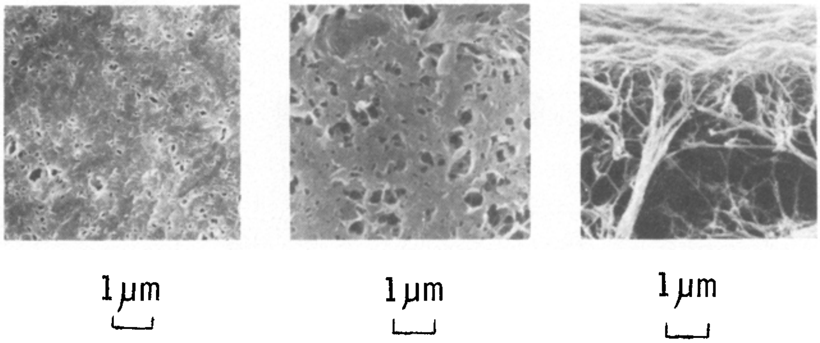


Figure 2. Effect of heat treatment time on permeation characteristics of polymer blend membranes from PVF_2 and PEG. Casting solution: PVF_2/THF/DMF=10/40/50 (wt%), PEG20000/PVF_2=25 (wt%); membrane preparation: 25 °C, 2 h; heat treatment temperature: 80 °C; feed: (○) pure water, (●) 1% aqueous solution of PVA 205; operating conditions: 40 °C, 2 kg/cm^2.

(ethylene glycol) before and after the heat treatment are shown in Figure 3. As can be seen from these photographs, the membrane after the heat treatment has larger pores. This fact suggests the results of permeation characteristics in Figure 2. Also photograph (c) in Figure 3 is the cross section of membrane



(a) (b) (c)

Figure 3. Scanning electron photographs of memranes from PVF_2 and PEG before and after heat treatment. (a): before heat treatment; (b); after heat treatment at 80 ^oC for 10 min; (c): cross section of membrane after heat treatment.

after heat treatment. The resulting membranes are asymmetric. The pores in the skin layer of membrane are not necessarily penetrated cylindrically and have some complicated network structure. Perhaps, the polymer solute, poly(vinyl alcohol) molecules, may be rejected by these polymer network parts in the pores.

References

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