P-16

Preparation and characterization of polyethersulfone microfiltration membrane by 2-methoxy ethanol nonsolvent additive

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Abstract

Microfiltration membranes were prepared from aromatic polyethersulfone (PES) polymer, using aprotic solvent (N-methyl-2-pyrrolidone, NMP) and non-solvent additive (2-methoxy ethanol, 2-ME) by the phase inversion co-process of the vapor-induced phase inversion (VIPI) and the nonsolvent-induced phase inversion (NIPI). According to the change of the additive amount, the solvent amount and the relative humidity, membrane characterization was studied. The non-solvent additive in casting solution played an important role in membrane morphology. During the vapor-induced phase inversion, the relative humidity led to water sorption on the surface of casting dope at which pore formation was generated. The prepared membranes were characterized by scanning electron microscope observations, measurements of capillary flow porometer and pure water flux (PWP). Also the thermodynamic and kinetic properties of membrane-forming system were studied through coagulation value, light transmittance and viscosity.

Introduction

The addition of organic or inorganic components as a non-solvent to a casting solution has been one of the significant techniques used in membrane preparation. It has been reported that organic and inorganic additives such as polyvinylpyrrolidone (PVP), polyethyleneglycol (PEG), water, ethanol, butanol, 2-methoxyethanol, acetic acid, maleic acid, piperazine, LiCl and $ZnCl_2$ and so on, act as pore-forming agents enhancing permeation properties. The characteristic of these non-solvent additives is water-soluble (Kim *et al.,* 1998).

In this study, microfiltration membrane was made by using the phase inversion co-process of VIPI and NIPI. PES/NMP/2-ME casting solution and water coagulant system was investigated at the viewpoint of membrane preparation and characterization. It will be discussed how the membrane morphology can be changed with the ratio of 2-ME to NMP in the casting solution and with the amounts of relative humidity in ambient air. Characterization of membrane will be observed through scanning electron microscopy (SEM) photographs, porometer analysis and pure water flux test.

Experimental

PES/2-ME/NMP casting solution consisted of PES 10~14 wt%, 2-ME 0~60wt%, and NMP 30~90 wt% mixture. The casting solution was poured on the non-woven fabric and cast with four sided applicator from Sheen Instruments Ltd. (England). Precipitating this casting film into a membrane was normally carried out by exposure to a non-solvent vapor, such as water vapor, which was absorbed on the exposed surface, and then by contacting the casting film with a non-solvent liquid (water) in a coagulation bath. After the precipitation, annealing of the prepared membrane into 50°C water bath, such as a post-treatment, was conducted during 24 hours. And then prepared membrane was washed with de-ionized water and dried in forced convection oven.

Results and discussion

The plots of coagulation value against the amount of polymer and the ratio of 2-ME to NMP are presented in Figure 1. The coagulation value was determined using water/NMP mixture of 25/75 and 50/50 (w/w %). Figure 1 shows that when the amount of polymer increases from 10 to 14 wt%, the coagulation value decreases. It indicates that the casting solution becomes thermodynamically less stable with increasing the amount of polymer. Also, the plots of coagulation value against the ratio of 2-ME to NMP from 0/90 to 60/30 (w/w %) in 10 wt% PES solution are presented in Figure 1. Figure 1 shows that the coagulation value decreases with increasing the 2-ME/NMP ratio from 0/90 to 60/30 (w/w %). It was found that the casting solution became slightly turbid with increasing the ratio of 2-ME/NMP ratio. When the casting solution with more than 60/30 (w/w %) of 2-ME/NMP ratio was used, the solution was not prepared as a homogeneous state. It indicates that the casting solution became thermodynamically less stable with increasing the ratio of 2-ME nonsolvent additive to NMP due to the increase in the concentration of 2-ME incompatible with PES membrane material instead of NMP solvent. The similar behaviors were observed in previous works (Kim *et al.*, 1998, Tai-Ping *et al.*, 1991, Kang *et al.*, 1991).

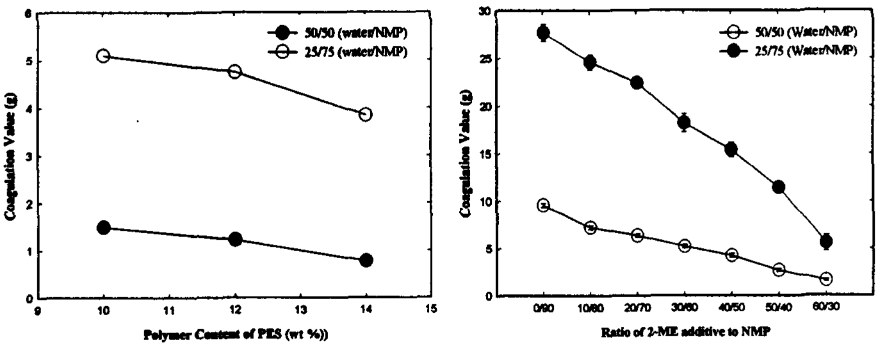

Figure 1 Coagulation value against the amount of polymer and the ratio of 2-ME to NMP

Light transmittance measurement technique, as the experimental technique of precipitation kinetics, was used by Smolder *et al.* (1992) and Mulder *et al.* (1991). In this study, light transmittance measurement technique was used. The delayed demixing of precipitation type is not observed. It is interesting to note that the instantaneous demixing of precipitation type is maintained under the thermodynamic less stable system produced by the addition of 2-ME. Another interesting point is that the overall precipitation rate also becomes slower with the increase in 2-ME/NMP ratio in PES solution. The exact reason is not yet clear.

According to Wang *et al.* (2000) and Park *et al.* (1999), water vapor can be easily absorbed into the polymer solution, initiate phase inversion, and result in surface pores. It was found that when the relative humidity in air increased, surface pores grew and the number of surface pore began to be plentiful in Figure 2.

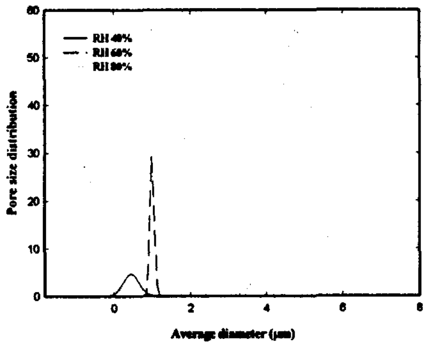

Figure 2 Pore size distribution against the relative humidity (RH) in 10/60/30 (w/w/w %, PES/2-ME/NMP)

Young *et al.* (1995) proposed that it is necessary for forming macrovoids that has a skin to limit the large amount of nonsolvent into the sublayer to introduce many nuclei formation. So to speak, porous toplayer can suppress the macrovoids formation of sublayer and result in porous, sponge-like structure. In an extreme case that the casting solution with 60/30 (w/w) of 2-ME to NMP was used, macrovoid-free and sponge-like cross-section was obtained in Figure 3 (a), (b). To the contrary, (c), (d) showed non-porous and macrovoid structure.

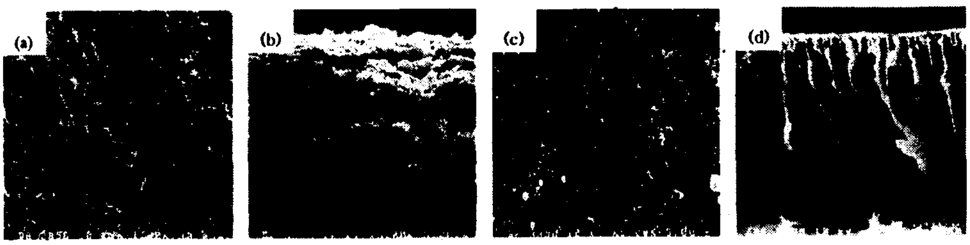

Figure 3 Effect of relative humidity and 2-ME nonsolvent additive on the formation of surface pores and cross-section (a) surface and (b) cross-section of 10/60/30, (c) surface and (d) cross-section of 10/20/70 (w/w/w %, PES/2-ME/NMP), at exposure time: 5 sec (magnitude: ×1.0K)

Conclusions

Thermodynamic and kinetic considerations were given for the effect of 2-ME as a pore-forming agent in the casting solution on the membrane-forming mechanism including the toplayer and the macrovoid in the co-process of VIPI and NIPI.

First, it is found that with increasing the ratio of 2-ME to NMP, and the amount of polymer, the coagulation value decreases; it means that the casting solution becomes thermodynamically less stable.

In the second place, sponge structure was superior to macrovoid structure for high permeate flux. A lot of pores at the surface of membrane needed to acquire the sponge structure. For making many surface pores, VIPI process, at which relative humidity was more than 50 %, was introduced. Also hydrophilic nonsolvent additive, such as 2-methoxyethanol, was required to draw water vapor into the solution to induce spontaneous emulsification and initiate the formation of cellular surface structure. The growth and coalescence of these emulsion drops would result in cellular surface pores when polymer was precipitated. Therefore, the more was the relative humidity at VIPI process, the larger were the pores of surface.

Porous toplayer could suppress the macrovoids formation of sublayer and result in porous, sponge structure. In an extreme case that the casting solution with 60/30 (w/w %) of 2-ME to NMP was used, macrovoid-free and sponge-like cross-section was obtained.

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References

T.-H. Young, L.-W. Chen (1995). Pore formation mechanism of membranes from phase inversion process, *Desalination*, **103**, 233-247.

C.A. Smolders, A.J. Reuvers, R.M. Boom, I.M. Wienk (1992). Microstructures in phase-inversion membranes. Part 1: Formation of macrovoids, *J. Membr. Sci.*, **73**, 259-275.

M. Mulder (1996). Basic Principles of Membrane Technology, *Kluwer*, Dordrecht.

J.-H. Kim, K.-H. Lee (1998). Effect of PEG additive on membrane formation by phase inversion, *J. Membr. Sci.*, **138**, 153-163.

D.M. Wang, T.T. Wu, F.C. Lin, J.Y. Hou, J.Y. Lai (2000). A novel method for controlling the surface morphology of polymeric membranes, *J. Membr. Sci.*, **169**, 39-51.

Hou Tai-Ping, Dong Sheng-Hua, Zheng Ling-Ying (1991). The study of mechanism of organic additives action in the polysulfone membrane casting solution, *Desalination*, **83**, 343-360.

H.C. Park, Y.P. Kim, H.Y. Kim, Y.S. Kang (1999). Membrane formation by water vapor induced phase inversion, *J. Membr. Sci.*, **156**, 169-178.