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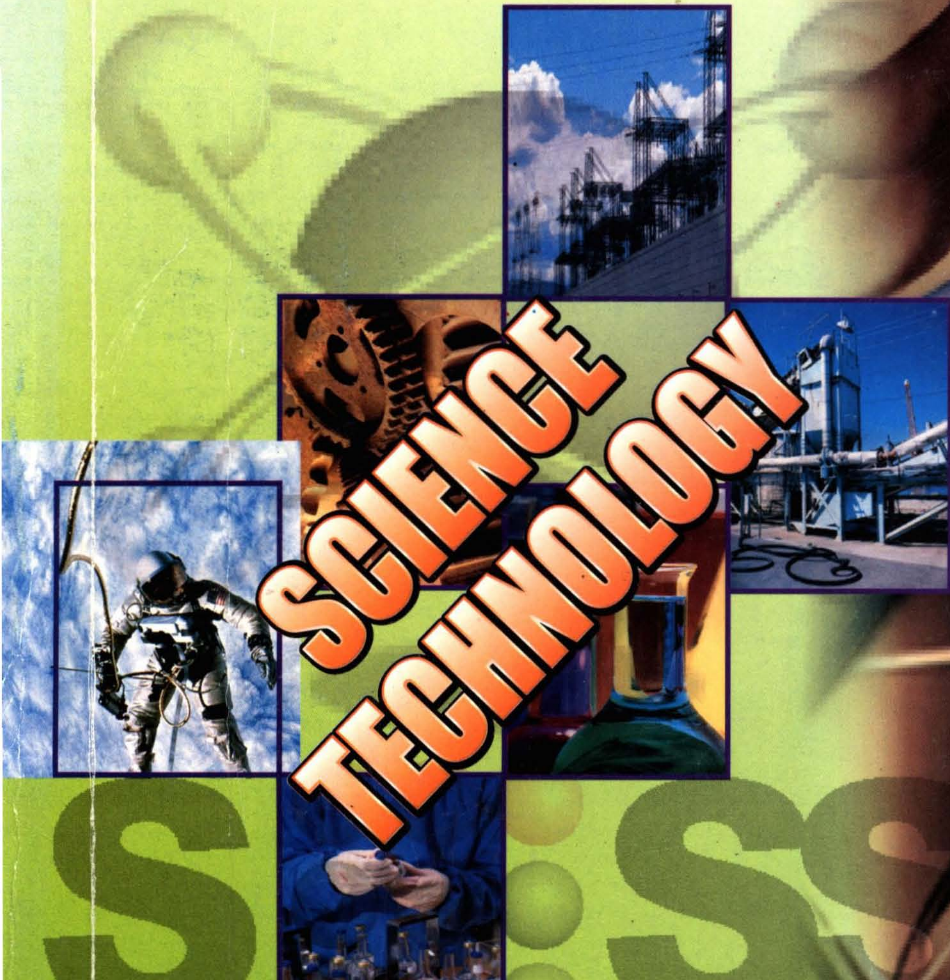

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Effects of Drying Temperature and Solvent Concentration on the Separation Properties of Polyamide 6 Membrane

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ABSTRACT

The effects of drying temperature and solvent concentration on the separation properties of polyamide 6 membrane were investigated. In this study, polyamide 6 membranes were prepared by casting 10-20 wt% solution of polymer in 85 wt% formic acid onto a glass plate and precipitation in water. The membranes prepared were dried for 1 hour at different temperatures ranging from 40 to 130 °C. The separation properties of the membranes were studied with binary water-ethanol mixtures consisting of 40 wt% ethanol. The drying temperature as well as the solvent concentration of PA 6 solution influenced the separation properties of PA 6 membrane. The separation of ethanol from water was optimum using membrane which was dried at 70°C. However, as the drying temperature increased, the extraction of ethanol decreased due to reduction in pore size. Similarly, as the solvent concentration decreased, the ethanol separation also decreased as a result of smaller pore size. These effects were confirmed by SEM micrographs.

Keywords: Polyamide 6, Water/Ethanol, drying temperature

Introduction

Membranes hac played a major and important role in the industrial, environmental and membrane science application (Winston et al. 1992). It is widely used in separation and purification process fields extending from liquid-liquid and liquid-gas separation processes. Membrane separation processes have been studied extensively as promising energy-saving separation techniques. A large number of polymers have been tested for the membrane materials. In particular, aliphatic polyamides, e.g. polyamide-3 (PA-3), polyamide-4 (PA-4), polyamide-6 (PA-6), polyamide-6,6 (PA-6,6), have been regarded as promising materials because of their excellent mechanical properties and commercial availability. Since aliphatic polyamides are highly crystalline and more or less hydrophobic material (PA-6, PA-6,6) numerous modified polyamides have been utilized for the separation of organic-organic or organic-water mixtures (Meier et al. 2000). Generally synthetic membranes are prepared at room temperature. However, polymer glasses prepared by cooling from the liquid state exhibit spontaneous changes in certain physical properties (Khulbe et al. 2004). Membrane formation depends to a large extent on structural arrangements and mobility of polymer molecules in lacquer or melts. A polymer solution may be defined as dispersion in a solvent system. Dispersion may be molecular (consisting of individual polymer molecules) or macromolecular (consisting of molecular aggregates) and its nature can vary with polymer type and concentration, molecular weight, temperature and solvent system (Khulbe et al. 2004). Different membrane preparation conditions lead to the situation when the membrane is amorphous, semicrystalline or liquid-crystalline. The most important factor determining the mechanism of molecules transport through a membrane is a supermolecular structure of the polymer, i.e. an arrangement of macromolecules in the polymeric membranes. Temperature and solvent concentration play a very important role during the process of membrane production. Both parameters control the growth of crystallites, and also the transportation of molecules through the membrane (Danch et al. 2004). Young *et al.* (2002) studied the effect of drying temperature on the morphology of poly(ethylene-co-vinyl alcohol) (EVAL), poly (vinylidene fluoride) (PVDF) and polyamide 66. It was found that membrane morphologies are strongly dependent on the drying temperature. This study investigates the effect of drying temperature and concentration of polyamide 6 solution on the separation property of polyamide 6 membranes.

Experiment

Materials 120

Polyamide-6 (PA-6; Mn 22.600 g/mol; Technyl R Polyamides) was purchased from Rhodia Engineering Plastics Co. Ltd. (Taiwan). Meanwhile, formic acid and pure ethanol both are analytical grade and were supplied by Systerm and Merck (Germany) respectively.

Membrane preparation

The membranes were prepared from casting solutions of PA-6 wt% in formic acid/water (85/15wt/wt) as the solvent (Cheng et al. 1995). PA-6/solvent ratio content (wt/wt) was varied at 10/90, 15/85 and 20/80 (wt/wt). Membranes were prepared by spreading the dope on a glass plate using a casting knife (Sheen Instruments, England). The solvent was allowed to evaporate at room temperature for 15 minutes, and then immersed in distilled water. The PA-6 membranes were then dried for an hour at various temperatures ranging from 40°C to 130°C in the drying oven (Table 1).

Separation of ethanol

Separation of ethanol was conducted based on experiment conducted elsewhere (Rzeszutek & Chow 1998). Equal volume of 100mL binary water-ethanol mixture consists of 60wt% water and 40wt% ethanol was placed in the test tube. The polyamide membranes prepared were carefully placed and secured on the opening of the test tubes. The test tubes were then inverted to put the samples in contact with the membranes and were shaken for 4 hours. The surface of the membrane was exposed to the sample solution. Duplicate experiments were conducted for each parameter tested.

The ethanol content in the solutions was analyzed using gas chromatography (Shimadzu GC-2010). The GC injection port and detector temperature was 200°C, the column (SGE BP20, Shimadzu) temperature was 40°C, and the carrier gas (helium) flow rate was approximately 3 ml min^{-1}. Scanning electron microscopic (SEM) studies of the polyamide membranes was recorded using an electron microscope model Leo VP 1430VP at an acceleration voltage of 1keV. Micrographs were taken from bottom view.

Table 1: Preparation conditions of the casting dopes

Polymer / Solvent (wt%) (PA-6 / Formic acid / Water)	Temperature (°C)
10 / 76.5 / 13.5	40
10 / 76.5 / 13.5	70
10 / 76.5 / 13.5	100
10 / 76.5 / 13.5	130
15 / 72.3 / 12.7	40
15 / 72.3 / 12.7	70
15 / 72.3 / 12.7	100
15 / 72.3 / 12.7	130
20 / 68 / 12	40
20 / 68 / 12	70
20 / 68 / 12	100
20 / 68 / 12	130

Results and Discussion

Effect of drying temperature on extraction property of PA-6 membrane

The effect of drying temperature on the separation properties of polyamide is shown in Figure 1. It is obvious that the drying temperature has a tremendous effect on the separation properties of PA 6 membrane. Within the range of temperature studied, the maximum separation of ethanol from water is observed when the membrane was dried at 70°C. Approximately 34% of ethanol was extracted when the membrane was evaporated at 70°C using 10wt% PA-6 solution. As the drying temperatures were further increased to 100°C and 130°C, the separation capability of ethanol decreased. A reduction in ethanol separation was also observed for the membranes, which were dried at 40°C. Shin et al reported the same trend on temperature effect for polyethersulfone membrane. The highest mean flow pore diameter was observed when the membrane was evaporated at 50°C. A reduction on the mean flow pore diameter was observed when temperature was below and above 50°C (Shin et al. 2005).

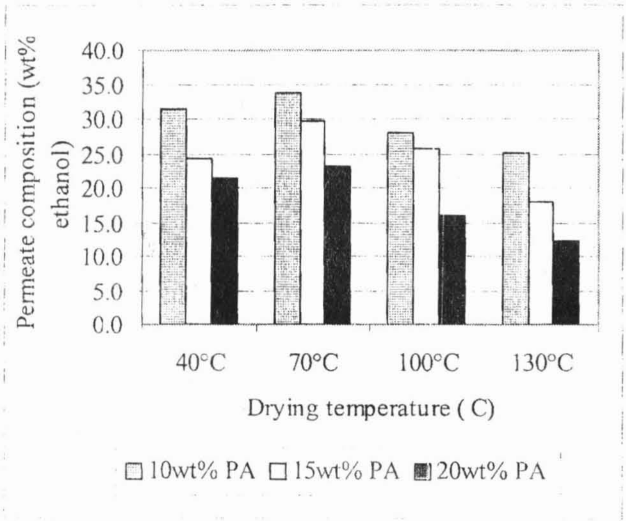


Fig 1: The effect of drying temperature on the separation properties of polyamide 6 membrane

Effect of solvent concentration on extraction property of the membrane

The influence of solvent concentration on the separation properties of the membrane at the ratio of PA6/solvent (wt/wt) at 10/90, 15/85 and 20/80 were studied. The effect of solvent concentration on the extraction of ethanol using PA6 membrane is illustrated in Figure 2. Within the range of temperature studied, the separation of ethanol decrease as the solvent concentration decreased as shown in Figure 2. When the amount of solvent in the casting solution was increased, the viscosity decrease and the diffusivity of the solvent increased (Shin *et al.*, 2005). Shin et al, 2005 showed that the different pore sizes of membrane were obtained, depending on the rate of diffusion. Low diffusion rates for high viscosity sample produced membrane with large pores, while high diffusion rates produced membranes with small pores

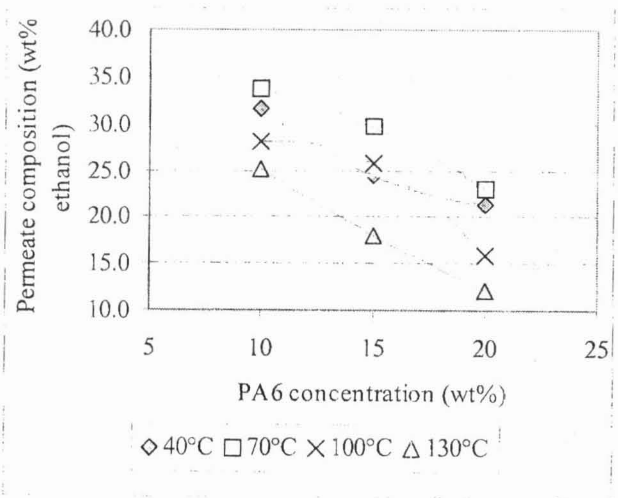


Fig. 2: The effect of PA-6/solvent concentration on the separation properties of polyamide 6 membrane

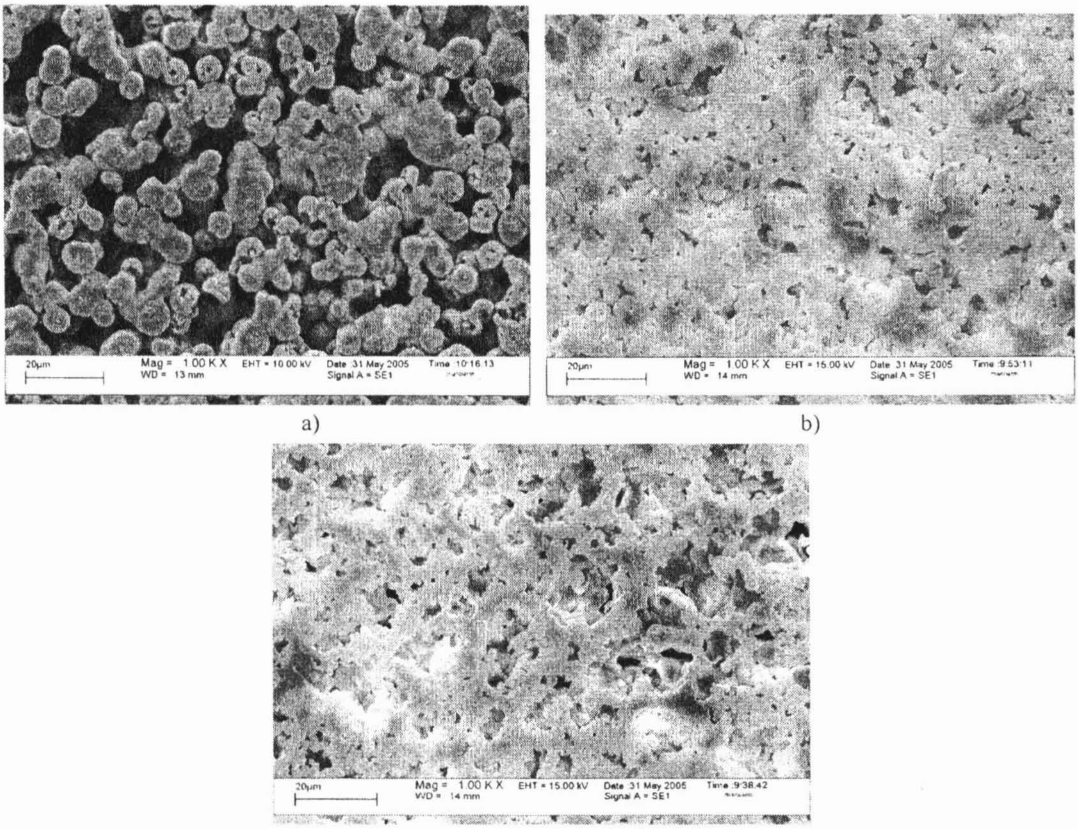
Scanning electron microscopy (SEM) analysis

SEM micrographs of the PA-6 membranes are displayed in Fig. 3 (a) and (b) which demonstrate the effect of temperature on 15wt% PA-6 dried at 70°C and 100°C respectively. Membrane dried at 70°C exhibits higher porous structure and bigger pore size compared to drying at 100°C. The rise in the drying temperature changed membrane structure from a particulate to a dense morphology. At elevated temperatures the crystallization was restricted for the membrane because the increase rate in the polymer concentration was fast relative to the time necessary for growth of nuclei (Dong *et al.*, 1998). As a result, higher drying temperature produces membrane with smaller pore size. This confirms the results of ethanol separation using PA-6 membrane in Fig. 1. Membrane with higher porosity and bigger pore size results in greater extraction of ethanol compared to membrane that has smaller pore size and denser.

Fig 3 (b) and (c) demonstrate the effect of solvent concentration which shows the surface of PA-6 membrane prepared using 85% and 90% solvent respectively. It is obvious that concentration of PA-6 solution has a tremendous effect on the porosity. The porosity of the membrane increase at high concentration of solvent as shown in Fig 3 (c). Higher porosity allows greater extraction of ethanol using the membrane as shown in Figure 1. Shin *et al.* (2005) reported the same trend on temperature effect for polyethersulfone membrane. The highest mean flow pore diameter was observed when the membrane was evaporated at 50°C. A reduction on the mean flow pore diameter was observed when temperature was below and above 50°C (Shin *et al.*, 2005).

Conclusion

The polyamide-6 membrane prepared by the phase-inversion process was capable of separating water/ethanol mixture. The drying temperature as well as the concentration of PA 6 solution influenced the separation properties of PA 6 membrane. The separation of ethanol was maximum when the membrane was dried at 70°C. Membrane prepared using higher solvent concentration also showed greater separation of ethanol. The porosity of the membranes prepared, increases with the solvent concentration. This was confirmed by the SEM micrographs.



a) b)

c)

Fig. 3: SEM micrographs demonstrating the surface of polyamide 6 membranes a) 15% PA6 dried at 70° C, b) 15wt% PA6 dried at 100°C, c)10wt% PA6 dried at 100°C

Acknowledgments

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