

PREPARATION OF ASYMMETRIC POLYETHERKETONE FLAT AND HOLLOW FIBER MEMBRANES FOR GAS SEPARATION USING ACETIC ACID BASED COAGULANTS*

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Abstract Membranes for gas separation have developed significantly in the last twenty years, however, there is still a need for high temperature and chemically resistant membranes that exhibit good selectivity and gas permeability. Our study examines the fundamental properties of polyetherketone (PEK, a thermally stable and chemically resistant polymer) membranes prepared using concentrated sulphuric acid (98% H₂SO₄) as the solvent. Non-solvents used in the work included acetic acid, ethanol, methanol, glycerol, and water. The concentration of the polymer solutions was chosen to be 20%. The membrane structures were examined using SEM, and the gas separation properties were measured using a lab-scale test rig. The results show that formation and control of membrane structures are complicated, and many preparation parameters affect membrane morphology and performance. Using appropriate conditions skinned sponge-like structured hollow fiber membranes could be made from PEK by using acetic acid as the internal coagulant. PEK hollow fibers spun from 20%PEK/H₂SO₄ solutions with 50% aqueous acetic acid as internal coagulant had selectivity for hydrogen/methane of around 40, implying a solution diffusion separation mechanism for gas separation without the need for fiber coating or after post-treatments.

Keywords: Polyetherketones; Membranes; Gas permeation; Internal coagulant effect; Morphology.

INTRODUCTION

Polyetherketone (PEK) with the structure given in Fig. 1 is a thermoplastic semi-crystalline polymer with the outstanding properties in terms of mechanical strength, creep-resistance and resistance to organic solvents, and these properties can be retained at very high temperature, up to 250°C^[1, 2]. These properties potentially make PEK an attractive high performance membrane material. Recent studies on the gas separation using PEK flat membranes emphasized the chemical modification of PEK polymer structure in determining relationships between the chemical structure of a polymer and its ensuing gas separation properties^[3–8]. Previous work on hollow fiber PEK membranes has been reported for potential use in ultra-filtration, micro-filtration and gas separation applications^[9–12]. However, only recently have we been able to produce hollow fiber membrane morphologies from PEK that are more suited to gas separation.

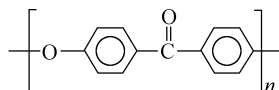


Fig. 1 Structure of the polyetherketone repeating unit

* This work was financially supported by the Engineering and Physical Sciences Research Council (EPSRC, No. GR/M56876).

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Received March 27, 2007; Revised May 21, 2007; Accepted May 23, 2007

Unlike the polyether ether ketone (PEEK) or modified PEEK^[13–16] and modified PEK^[3–8] or other polymers which could be soluble in common solvents, PEK with the structure given in Fig. 1 is insoluble in conventional organic solvents at room temperature and only dissolves in very strong acids such as liquid hydrogen fluoride, methanesulphonic acid (MeSO₃H), trifluoromethane-sulphonic acid and concentrated sulfuric acid (H₂SO₄). Thus, generally, when PEK hollow fibers are produced (by phase inversion in water) they possess a finger-like macrovoid structure because of the large solvent non-solvent interactions. These macrovoids are evident in PEK hollow fiber cross sections reported previously, and the macrovoids have an unfavorable influence on the gas separation performance of the fibers^[13]. It is well established that appropriate non-solvent selection for both internal and external coagulant is critical to the performance of the hollow fiber membranes for gas separation. Indeed, these are vital in determining the membrane morphology and ultimately performance of the hollow fiber membranes. This study describes an investigation of a process for making PEK hollow fibers and flat membranes suitable for gas separation and properties of the resulting membranes.

EXPERIMENTAL

Solution Preparation

The polyetherketone (PEK) used in this study was obtained from ICI (Viktrex-PEK, MV 0.392) with the structure given in Fig. 1, which was dried for 24 h at 100°C under vacuum prior to dissolution. Analytical reagent grade concentrated sulfuric acid (98% H₂SO₄) and acetic acid (AA) were supplied by Fisher scientific company. The solvent of 98% H₂SO₄ was first added into a clear reaction vessel which was placed in a water bath at 50°C, then fixed quantity of PEK was added to the solvent. After stirring the mixture of solvent with polymer at 300–500 r/min for 5 h, a clear red solution of PEK in certain concentration was obtained without detected sulfonation.

The Measurement of Precipitation Values (PVs)

The term of precipitation values (PVs) has been previously defined as the grams of non-solvent required to cause visual turbidity in a solution containing 100 g of solvent and 2 g of polymer^[17, 18]. For the PEK/solvent system, the polymer solution containing 100 g solvent and 2 g of PEK was placed in a conical flask with stirring. And the selected non-solvent was added at 0.1 mL/min until the original homogeneous solution became cloudy visually. The quantity in grams of the non-solvent required to make the polymer solution turbid was obtained by converting the measured volumes of used non-solvent into grams according to their density at 20°C. Then the PV can be calculated from the amount of non-solvent used and the polymer solution in the bottle.

Precipitation Time of Flat PEK Membranes

The term “precipitation time” was defined to describe qualitatively the phase inversion process. Put 1.0 g polymer solution on glass plate, moved the metal rod which was designed to cast a thin film with fixed thickness of 250 µm, then a wet film was prepared on glass plate. Seconds later, glass plate was immersed into the coagulant with fixed volume of 100 mL^[19, 20]. The precipitation time was recorded as the time period from when the nascent cast film (with wet thickness 250 µm) was immersed into the coagulation bath (100 mL), to when the film separated completely from the glass plate. In other words the shorter the “precipitation time”, the more rapidly the polymer precipitates in the coagulant and separates from the plate. After the membranes had separated from the glass plate, they were removed from the bath and washed in water for one week, dried at room temperature for 24 h and then stored in a desiccator before use.

Hollow Fiber Spinning

Asymmetric PEK hollow fibers were spun using a dry-jet wet spinning process^[21, 22] at room temperature as illustrated in Fig. 2. The spinning dope was prepared by stirring dried polyetherketone chip in concentrated sulfuric acid for 5 h at 50°C to form a homogeneous solution of 20 wt% PEK of viscosity 120 Pa·s as measured at 25°C using a Haake Rotovisko RV12 viscometer with measuring drive M1500. The spinning dope was degassed under vacuum and then extruded using a nitrogen pressure of 0.55 Pa through a tube-in-orifice type

spinneret. The spinneret of a single hole tube in orifice type had an orifice outer diameter of 1000 μm and an inner diameter of 510 μm , respectively. The bore fluid was injected using a precision piston pump (DESAGA GmbH KP2000) at the desired rate. The fiber then passed vertically via an air gap of 9 cm before entering the 2 m long coagulant bath. Water or aqueous acetic acid solutions were used as internal coagulants, and pure water was used as the external coagulant. The fiber was then taken from the coagulant bath by low-friction guide rollers and collected onto a drum as a non-overlapping band of filaments whilst being continuously washed with water. The wind-up speed was controlled to match the fiber free-falling velocity after extrusion so that no elongation stresses were applied to the nascent fibers. The hollow fiber filaments were cut from the drum to give hollow fibers of length 70 cm. The cut fibers were washed in a water bath for two weeks. The washing water was changed twice daily for over this period. The fibers were, then transferred to an acetone bath for 2 h and then dried at room temperature for 24 h before testing for permeation behavior.

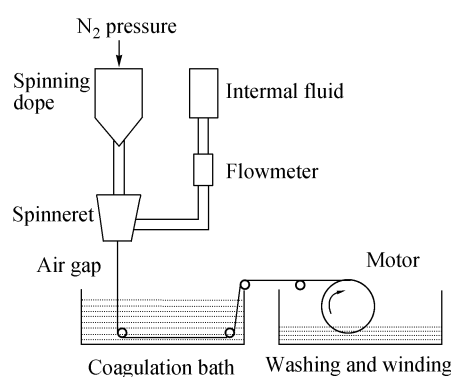


Fig. 2 Schematic diagram of hollow fiber spinning apparatus

SEM Investigation

The cross-sectional membrane morphologies of the fibers and films were examined with a Camscan 340 scanning electron microscopy (SEM). To investigate the membrane structure, the membranes were immersed in liquid nitrogen for 5 min, fractured and sputtered with gold.

Module Fabrication and Gas permeation Tests

Gas permeation measurements were carried out using hydrogen, methane and carbon dioxide. Hollow fibers were mounted into a module that was then fixed into the permeation chamber of the testing rig assembly (Fig. 3). The modules consisted of a bundle of ten fibers (each being of length of 20 cm) at which one end was blocked with a small copper end cap and glued in with epoxy resin. This left the other end of the potted and cut bundle open for permeation.

The rate of flow of single gas (H_2 , CH_4 and CO_2) through the flat membrane or hollow fiber module was measured at room temperature using lab-scale gas permeation rigs described previously^[19, 20]. The permeation rate of gases through the flat and hollow fiber membranes was determined using the following equation:

$$P' = \frac{Q_i}{\Delta P \cdot A}$$

P' is the permeation rate of the membranes in gas permeation unit of GPU where one GPU is equal to $7.50 \times 10^{-10} \text{ cm}^3/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$; Q_i is the volume flow rate of gas (cm^3/s), ΔP is the pressure differential across the membrane, and A is the membrane surface area in cm^2 . The ideal separation factor of gas A over gas B for flat film or hollow fiber is given by the following equation:

$$\alpha_{A/B} = \frac{P'_A}{P'_B}$$

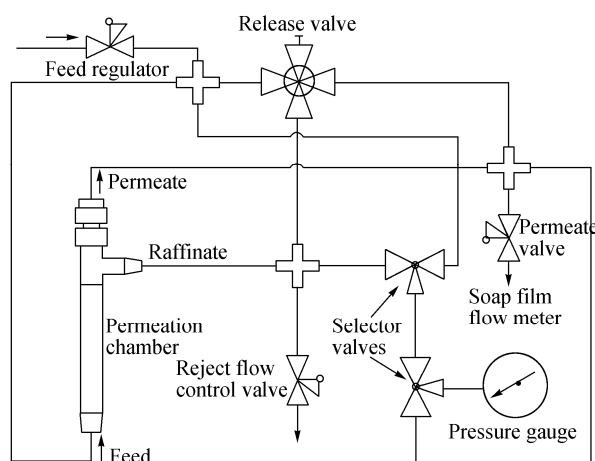


Fig. 3 The permeation performance test rig

RESULTS AND DISCUSSION

PVs of PEK/H₂SO₄/Non-solvent Systems

The non-solvents used in the phase inversion process greatly affect the physical and gas permeation properties of as-spun fibers. Studies on the phase separation of a polymer/solvent/non-solvent system provided information for the choice of suitable coagulant applied in the precipitation process. The PV of a non-solvent in a polymer/solvent system can be used as a measure of the non-solvent tolerance of the polymer/solvent solution system. The lower the compatibility of the non-solvent and the polymer the greater the tendency for polymer aggregation and precipitation, which leads to lower PVs^[17]. Using Teo's method^[17, 18], the phase-separation behavior of PEK/solvent/non-solvent systems was investigated by measuring their precipitation values (PV) using water, glycerol, glycol, methanol, ethanol and acetic acid (AA) as the non-solvents, and the results are presented in Table 1.

Table 1. PVs (g) of non-solvents in the 2%PEK/H₂SO₄ system

Non-solvent	Water	Glycerol	Glycol	Methanol	Ethanol	Acetic acid
PVs (g)	16.0	20.0	22.3	25.9	36.4	57.2

The PVs for the non-solvents increased in the order water < glycerol < glycol < methanol < ethanol < acetic acid. The PV for the water is much lower than that of the alcohols and acetic acid, which suggests (as expected) that water is a much stronger non-solvent compared to the alcohols and acetic acid for the PEK/H₂SO₄ system, and thus PEK/H₂SO₄ polymer solutions will have a low tolerance to water. The results can also be rationalised by examining the solubility parameters of the non-solvents (Table 2)^[23]. It is clear that increasing PVs are consistent with the decreasing order of solubility parameters (δ) for the non-solvents, especially with the decreasing order of hydrogen-bonding component of the solubility parameters (δ_h).

Table 2. Hansen's solubility parameters of the non-solvents (J·cm⁻³)^{0.5[23]}

Non-solvent	Water	Glycerol	Glycol	Methanol	Ethanol	Acetic acid
δ_p	31.3	12.1	11.0	12.3	8.8	8.0
δ_h	34.2	29.3	26.0	22.3	19.4	13.5
δ_d	12.3	17.4	17.0	15.4	15.8	14.5
δ_t	48.0	36.2	33.0	30.0	26.5	21.4

δ_p , δ_h , δ_d and δ_t represent polar, hydrogen bonding, dispersion and total cohesion parameter, respectively.

The polar interaction of the polymer/solvent/non-solvent system depends mainly on their hydrogen-bonding ability represented by the δ_h component of the solubility parameter. The non-polar interaction depends

on the hydrophobic nature of the component^[17]. It was seen that non-solvents with larger δ_h values (water, glycerol, glycol, methanol and ethanol) have relatively low PVs which is a direct evidence of the weak interaction between PEK and these non-solvents. In contrast non-solvents with relatively lower δ_h values have lower hydrogen-bonding ability and exhibit some non-solvent/polymer compatibility and thus gave higher PVs^[17].

Precipitation Time and SEM Investigation of Flat Membranes

In PEK/H₂SO₄ solution systems, water is the simplest coagulant to make flat or hollow fiber membranes. However, the membranes prepared from PEK/H₂SO₄/water systems always have finger-like structures in the cross section of membranes^[12, 13]. To overcome this barrier, other non-solvents were chosen in an attempt to prepare asymmetric membranes with membrane morphologies deemed to be suitable for good gas separation performance. In this study, water, acetic acid, ethanol/water and acetic acid/water mixtures were used as coagulants to make flat PEK membranes. The relatively high PVs were obtained (Table 1) when acetic acid and ethanol-based coagulants were used, implying a high non-solvent tolerance of PEK/H₂SO₄ solution to acetic acid and ethanol, and this therefore reduces the PEK precipitation rate. It is well established that large finger-like structures are associated with fast precipitation rates whereas the slow precipitation rates tend to produce cellular porous sponge structures.

Table 3 lists the results of precipitation time of flat membranes in different coagulants. The various precipitation times corresponded to different liquid-liquid demixing procedures, and this results in various membrane structures and gas transport properties^[17, 18, 24–27]. Examination of precipitation time of flat membranes in different coagulants gave useful information regarding the phase inversion process of PEK membranes.

Table 3. The precipitation time (PT) of 20%PEK in various coagulants

Coagulants	PT (min)	Coagulants	PT (min)
Water	1.34		
10% ethanol	1.77	10% AA	1.76
30% ethanol	1.40	30% AA	2.01
50% ethanol	1.70	50% AA	2.30
70% ethanol	2.73	70% AA	3.63
90% ethanol	4.58	90% AA	16.1
Ethanol	7.50	Acetic acid	58.0

Basically PEK solutions precipitate very rapidly in water. When ethanol and acetic acid were used as coagulants, it took a longer time to precipitate PEK from solution as expected from the PVs determined earlier. The precipitation time order was consistent with the order of PVs, in that non-solvent with high PVs also took longer to produce PEK cast film. Thus it appears that the use of PVs and precipitation time can at best be used as indicators for the prediction of membrane structures. If mixture of acetic acid/water was used the precipitation time was shorter than that of pure acetic acid but longer than that of pure water. In other words the precipitation time was extended when the concentration of acetic acid was increased. The same trend was found in precipitation time for the PEK/H₂SO₄ system when 70% ethanol concentration and above was used as coagulant though the precipitation time changed little at below 70% ethanol concentration.

Figures 4 and 5 show the cross-sectional structures of flat membranes prepared from 20 wt% PEK/H₂SO₄ system when various non-solvents were used as coagulants. The structure of the membrane in Fig. 4 (pure water coagulant) shows a typical finger-like morphology. A systematically changing from pure water through a series of water/acetic acid concentrations (Fig. 5) shows that the membrane structure can be tuned. PEK membrane structures gradually changed from large finger-like macrovoids to smaller void and the greatest proportion of sponge-like structures were seen in the cross sections when high concentrations of acetic acid were used. This confirms that slow precipitation rates (long precipitation times) result in more porous sponge structures^[28]. However, pure acetic acid as coagulant again led to the formation of large voids in the cross section. This is because when using pure acetic acid as coagulant, the precipitation rate and the exchange rate between solvent

and non-solvent were so slow that the nascent film still contained a lot of solvent H_2SO_4 when the membrane has separated from the glass plate. In the following water-washing treatment, the water would get into the film quickly to exchange the inside H_2SO_4 out. This would give the film small sponge structure plus large voids above.

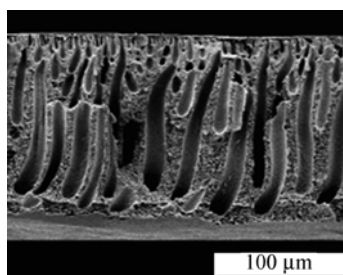


Fig. 4 The cross-section morphology of flat membrane prepared from 20% PEK with water as coagulant

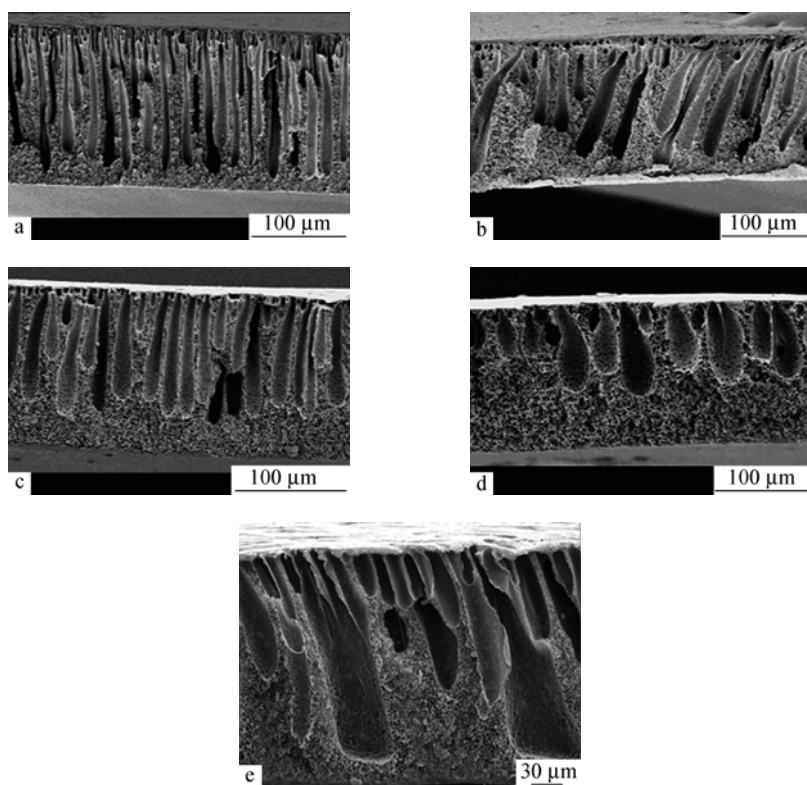


Fig. 5 The cross-section morphologies of flat membranes prepared from 20%PEK with aqueous acetic acid solution in various concentrations as coagulant
Coagulant: a) 30% AA in water; b) 50% AA in water; c) 70% AA in water; d) 90% AA in water; e) 100% AA

Interestingly PEK flat membranes prepared from ethanol or ethanol/water mixtures possessed large voids (finger-like structures) regardless of the concentration of ethanol in water (Fig. 6). The figure-like structures increased with increasing ethanol concentration (above 70%). It is clear that other chemical characteristics of the coagulant influence the morphology to a great extent. In general speaking, volatile ethanol has fast diffusion rate to get into the film so that the precipitation of PEK from solution was fast, meanwhile a lot of solvent H_2SO_4 and

ethanol still were kept in the film before the film was immersed and washed in the water. That water mixed with ethanol and H_2SO_4 very fast during the post-treatment intended to give large figure-like structures.

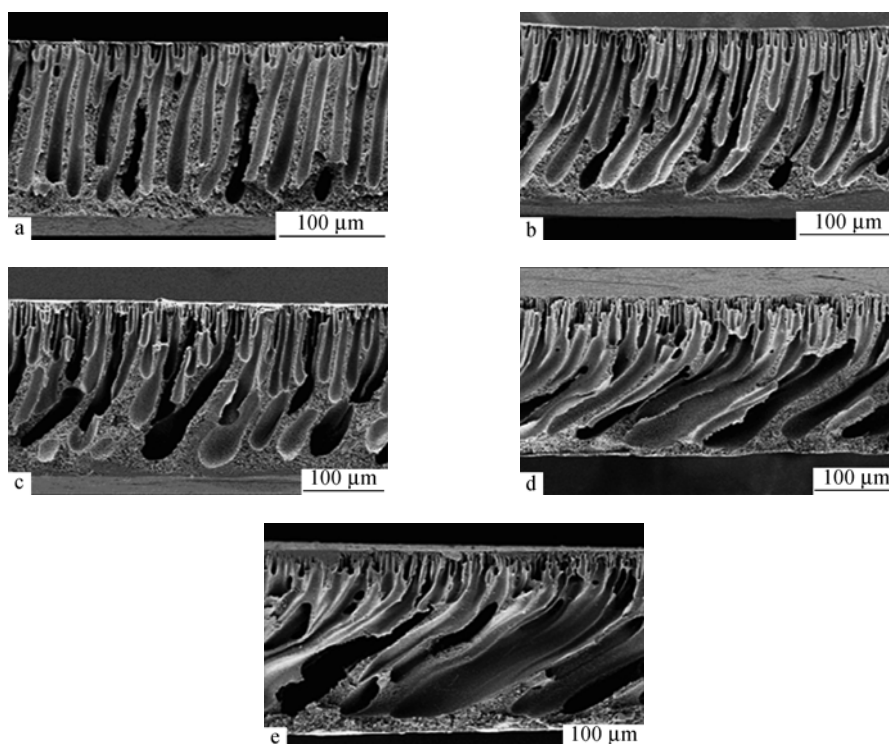


Fig. 6 The cross-section morphologies of flat membranes prepared from 20% PEK with aqueous ethanol solution in various concentrations as coagulant
Coagulant: a) 30% ethanol in water; b) 50% ethanol in water; c) 70% ethanol in water; d) 90% ethanol in water; e) 100% ethanol

Gas Permeation Properties of Asymmetric Flat Membranes

Table 4 summarizes the gas permeation rates of flat membranes prepared from 20% PEK/ H_2SO_4 polymer solutions using water, acetic acid and ethanol at a range of concentration from 10%–100% as the coagulants. The gas permeation rates of the asymmetric flat membranes increased as the concentration of acetic acid or ethanol increased, and correspondingly gas selectivities were decreased. The membrane produced when water was used as the coagulant had the lowest gas permeation rate for methane and the highest gas selectivity with $\alpha_{\text{H}_2/\text{CH}_4}$ of 14.1. This strongly suggests that this membrane has a dense skin layer with only a few defects as solution-diffusion behavior rather than Knudsen is beginning to dominate the separation process. On the other hand, the gas permeation properties of the membranes produced using pure acetic acid or pure ethanol as coagulant were much higher than those of the other membranes. However, the selectivity of the membranes was low and corresponds to the separation factors expected from Knudsen diffusion.

Table 4. Gas permeation properties of flat membranes prepared from 20% PEK

Coagulant	P'_{H_2} (GPU)	P'_{CH_4} (GPU)	P'_{CO_2} (GPU)	α_{H_2/CH_4}	α_{CO_2/CH_4}
Water	2.39	0.17	1.13	14.1	6.65
10% ethanol	2.09	0.60	0.93	3.47	1.54
30% ethanol	4.70	0.83	1.41	5.67	1.69
50% ethanol	4.60	1.13	1.70	4.07	1.50
70% ethanol	7.52	1.74	2.08	4.32	1.20
90% ethanol	7.60	2.66	2.82	2.86	1.06
Ethanol	841	377	218	2.23	0.58
10% acetic acid	2.27	0.24	1.05	9.46	4.38
30% acetic acid	3.17	0.80	1.32	3.96	1.65
50% acetic acid	5.52	2.01	2.38	2.75	1.18
70% acetic acid	5.02	1.61	2.20	3.12	1.37
90% acetic acid	11.31	6.10	4.56	1.85	0.75
Acetic acid	3264	1258	717	2.59	0.57

SEM Investigation of PEK Hollow Fiber Membranes

From the flat membrane studies it was clear that PEK membrane morphologies and membrane properties were tunable with different coagulant compositions. However, in hollow fiber production both internal and external coagulants can be different and this provides an opportunity to optimise both the selective skin layer and the supporting membrane substructure. Examination of the PEK flat membranes led to the belief that PEK hollow fibers with porous sponge substructures and selective skin layers could be produced if aqueous acetic acid was used as the internal coagulant and water used as the external coagulant. Hollow fiber membranes were thus spun from 20% PEK/H₂SO₄ solutions using aqueous acetic acid solution as internal coagulants and pure water as external coagulant. Figure 7 shows the cross-sectional structures of the hollow fibers produced.

When water is used as the internal coagulant, long finger-like structures are present close to the outer and inner surface of the PEK hollow fiber, and sponge-like structures are limited to a small portion of the fiber. This resulting finger structure corresponds to that expected if rapid precipitation occurs at both the outer and inner fiber walls. In general changing coagulant from water to aqueous acetic acid resulted in a reduction of inner finger-like structures in the hollow fiber walls with increasing acetic acid concentration. It is also clear that the internal bore diameter of the hollow fiber changes with the different internal coagulant composition at the same polymer extrusion rate and internal injection rate. It might be expected that during fiber formation, the internal acid coagulant, due to its lower precipitation power (compared to water) expands the surrounding polymer solution fluid stream to a greater degree than a pure water coagulant. Indeed, this is the case as shown by the hollow fiber cross sections seen in Fig. 7(c) and Fig. 7(d). However, very high acetic acid concentrations (more than 90%) were found to be highly unfavourable due to the formation of 'pleated' non-circular lumens (Fig. 7e). Under these conditions the fiber is unable to form a suitably stabilised internal skin structure and thus collapses or expands internally by transverse stresses produced by large differences in the rate of formation of the inner and outer membrane skin layers. An optimised PEK hollow fiber structure would have an ultra-thin 'defect free' separating dense layer, with a highly porous substructure acting as a strong but highly permeable support wall. Therefore appropriate choice of internal coagulant could produce PEK hollow fibers with structures approaching that of an ideal fiber.

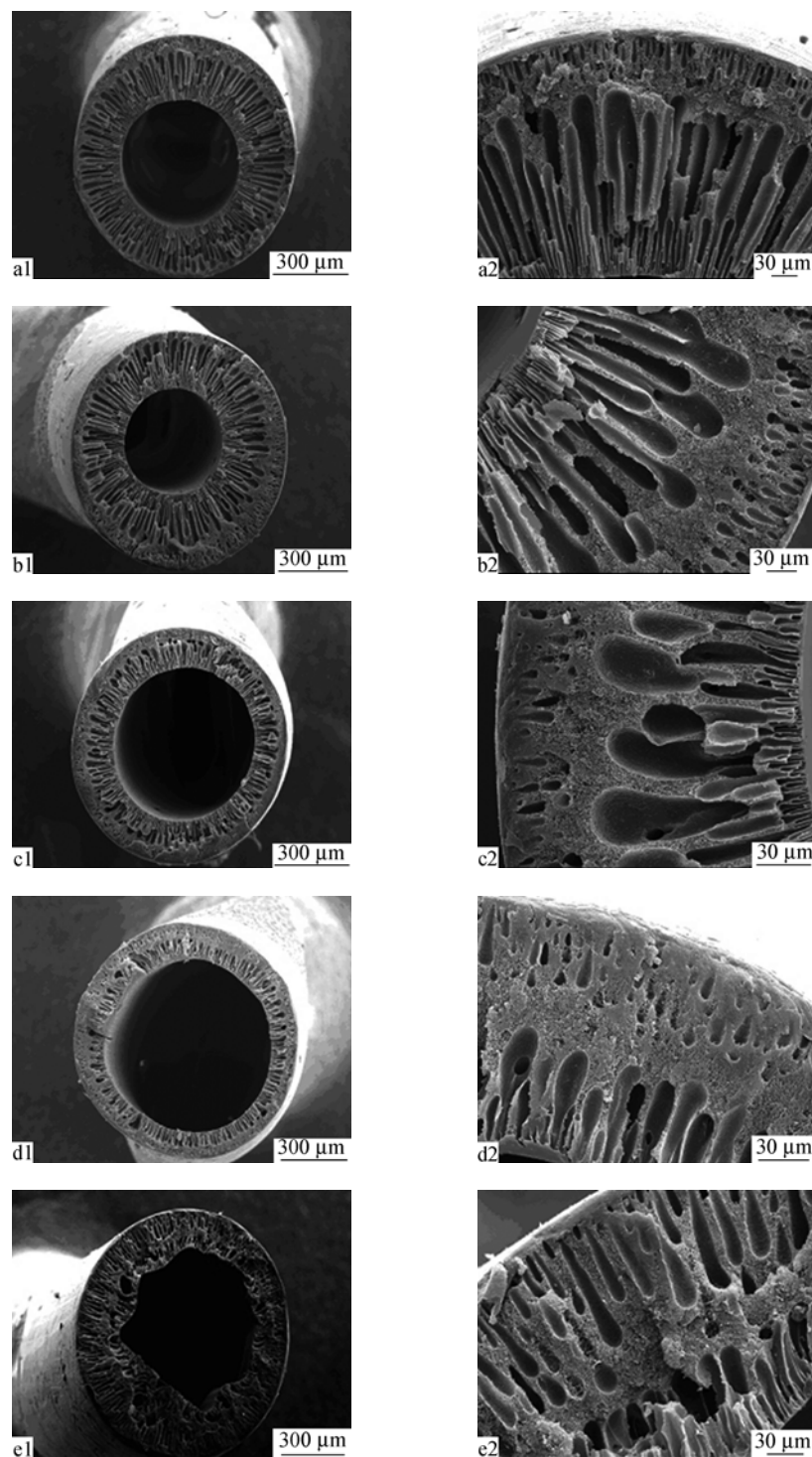


Fig. 7 The cross-section morphologies of hollow fibers spun from 20% PEK with water (a) or aqueous acetic acid as internal coagulants: (b) 10% acetic acid, (c) 50% acetic acid, (d) 70% acetic acid, (e) 90% acetic acid
 1) Cross-section of the hollow fiber; 2) The magnified segment of the hollow fiber;
 Internal coagulant injection rate: a) 30 mL·h⁻¹; b) 30 mL·h⁻¹; c) 30 mL·h⁻¹; d) 30 mL·h⁻¹; e) 10 mL·h⁻¹

Gas Permeation Properties of PEK Hollow Fiber Membranes

The gas permeation rates of PEK hollow fiber membranes spun from 20% PEK using various internal coagulant and bore fluid injection rates are given in Table 5. The presence of more acetic acid in the internal coagulant did not significantly influence the fiber gas permeability. However if higher concentrations of acetic acid are used *e.g.*, 70% increases in permeation rate occur. This implies that higher acetic acid concentration induces a higher porous inner substructure that in turn leads to higher gas flux.

Table 5. Gas permeation properties of PEK hollow fibers at different internal coagulant parameters

Internal coagulant	Injection rate (mL·h ⁻¹)	P'_{H_2} (GPU)	P'_{CH_4} (GPU)	P'_{CO_2} (GPU)	α_{H_2/CH_4}	α_{CO_2/CH_4}
Water	30	2.18	0.158	0.461	13.8	2.92
10% AA	30	3.92	1.05	0.733	3.73	0.70
30% AA	30	5.82	1.45	1.06	4.01	0.73
50% AA	30	4.95	0.126	0.972	39.3	7.71
70% AA	30	41.4	13.0	8.34	3.18	0.64
90% AA	10	589	259	169	2.27	0.65

The gas permeation rates for hydrogen gas did not change greatly when 0–50% acetic acid was used as the internal coagulant. However the selectivity was increased for H₂/CH₄ to 39.3. We suggest for this system that a critical coagulant composition exists that aids densification of the internal skin layer of the hollow fiber and thus improves the gas separation performance. As it can be seen in Table 5 maintenance of hydrogen permeation rates with enhanced H₂/CH₄ separations occur when 50% acetic acid is used as the internal coagulant. This could correspond to the gas separation mechanism changing over from one of Knudsen flow to one of solution-diffusion.

Increasing the internal coagulant injection rate led to a large decrease of gas permeation rates with slight increases in selectivity as shown in Table 6. We believe this is due to a denser, more compact inner membrane being produced at increasing internal coagulant injection rates.

Table 6. Gas permeation properties of PEK hollow fibers with 70% acetic acid as internal coagulant at various internal coagulant injection rates

Injection rate (mL·h ⁻¹)	P'_{H_2} (GPU)	P'_{CH_4} (GPU)	P'_{CO_2} (GPU)	α_{H_2/CH_4}	α_{CO_2/CH_4}
10	109	49.0	33.1	2.22	0.68
30	41.4	13.0	8.34	3.18	0.64
90	6.61	1.29	2.52	5.12	1.95

CONCLUSIONS

PEK hollow fiber membranes were successfully spun using aqueous acetic acid as internal coagulant. Improved morphologies for gas permeation in flat and hollow fiber forms were obtained when aqueous acetic acid was used as the internal coagulant as opposed to using water. For this system a critical internal coagulant composition appears to exist. In going from 0–70% acetic acid concentration only slight changes in hydrogen permeation rate occurred, but large improvements in hydrogen/methane selectivity were seen when 50% acetic acid was used as the internal coagulant. Beyond 50% acetic acid concentration gas selectivities drop with only slight increases in hydrogen permeation rates. The PVs of several alcohols (glycerol, glycol, methanol, and ethanol), acetic acid and water in polyetherketone/H₂SO₄ system, and PTs of 20% PEK in various coagulants were measured. The suitable precipitation value (PV) and precipitation time (PT) had been shown to be a useful tool to evaluate suitable coagulants and conditions to make asymmetric membranes.

REFERENCES

- 1 McGrail, P.T., *Polym. Int.*, 1996, 41: 103
- 2 Staniland, P.A., "Comprehensive Polymer Science—the Synthesis, Characterization, Reactions & Applications of Polymers", ed. by Eastmond, G.C., Ledwith, A., Russo, S. and Sigwalt, P., Pergamon Press, New York, 1995, p.483
- 3 García, C., Tiemblo, P., Lozano, A.E., de Abajo, J. and de la Campa, J.G., *J. Membr. Sci.*, 2002, 205: 73
- 4 Maier, G., Wolf, M., Bleha, M. and Pientka, Z., "Polymer Membranes for Gas and Vapor Separation, Chemistry and Materials Science in ACS symposium series 733", ed. by Freeman, B.D. and Pinnau, I., Oxford University Press, Oxford, 1999, p.256
- 5 Maier, G., *Angew. Chem. Int. Ed.*, 1998, 37: 2960
- 6 Xu, J., Wang, Z. and Chen, T., "Polymer Membranes for Gas and Vapor Separation, Chemistry and Materials Science in ACS symposium series 733", ed. by Freeman, B.D. and Pinnau, I., Oxford University Press, Oxford, 1999, p.269
- 7 Wang, Z., Chen T. and Xu, J., *J. Appl. Polym. Sci.*, 1997, 64: 1725
- 8 Wang, Z.G., Chen T.L. and Xu, J.P., *Chem. J. Chin. Un.-Chin.*, 1996, 17: 1796
- 9 Colquhoun, H.M., Roberts, K., Simpson, A.F., Taylor, T.M.C., East, G.C., McIntyre J.E. and Rogers, V., "3rd International Conference on Effective Membrane Processes-New Perspectives", ed. by Patterson, R., Mechanical Engineering Publications Limited, Bath, 1993, p.371
- 10 Colquhoun, H.M. and Taylor, T.M.C., 1990, *Euro. Pat.*, 0,382,356 A2
- 11 Sonnenschein, M.F., *J. Appl. Polym. Sci.*, 1999, 72: 175
- 12 Ying, S., Rogers-Gentile, V. and Brown, P.J., *J. Text. Inst.*, 1999, 90: 30
- 13 Tasselli, F., Cassano, A. and Drioli, E., *Separation and Purification Technology*, 2007, 57(1): 94
- 14 Jansen, J.C., Buonomenna, M.G., Figoli, A. and Drioli, E., *Desalination*, 2006, 193: 58
- 15 Macchione, M., Jansen, J.C. and Drioli, E., *Desalination*, 2006, 192: 132
- 16 Liu, B.J., Dai, Y., Robertson, G.P., Guiver, M.D., Hu, W. and Jiang, Z.H., *Polymer*, 2005, 46: 11279
- 17 Wang, D., Li, K. and Teo, W.K., *J. Appl. Polym. Sci.*, 1999, 71: 1789
- 18 Wang, D., Li, K. and Teo, W.K., *J. Membr. Sci.*, 1995, 98: 233
- 19 Brown, P.J., Thesis, The University of Leeds, UK, 1991
- 20 Senn, S., Thesis, The University of Leeds, UK, 1988
- 21 Meng, B., Yang, N., Tan, X. and Zhang, B., *Chinese J. Polym. Sci.*, 2005, 23(1): 75
- 22 Li, H., Li, X., He, X., Li, X., Cao Y. and Yuan, Q., *Acta Polymerica Sinica(in Chinese)*, 2007, (3): 250
- 23 Marton, F.M., "Handbook of Solubility Parameters and Other Cohesion Parameters", CRC press, London, 1988, p.159
- 24 Shieh, J.J. and Chung, T.S., *J. Membr. Sci.*, 1998, 140: 67
- 25 Deshmukh, S.P. and Li, K., *J. Membr. Sci.*, 1998, 150: 75
- 26 Han, M.J. and Bhattacharyya, D., *J. Membr. Sci.*, 1995, 98: 191
- 27 Machado, P.S.T., Habert, A.C. and Borges, C.P., *J. Membr. Sci.*, 1999, 155: 171
- 28 Brown, P.J., Ying, S. and Yang, J., *AUTEX Research J.*, 2002, 2: 101