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Study on the effect of spinning conditions and surface treatment on the geometry and performance of polymeric hollow-fibre membranes¹

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Abstract

Hollow-fibre membranes were prepared by the wet-dry spinning technique from polyether sulfone (PES). The effect of spinning conditions such as the flow-rate of the internal coagulant and the flow-rate, composition and temperature of the polymer solution on the geometry and performance of hollow fibres was studied. In particular, five different ratios of pore former/polymer covering the range 0.2–1.0 were investigated while the polymer content was kept constant. Since the viscosity of the spinning dope affects the morphology of the hollow-fibre membrane, hollow fibres were prepared at different temperatures of the spinning dope from 25 to 60°. By scanning electron microscopy (SEM) two layers sandwiching a finger-like cavity structure were observed. Also, the surface on the bore side of the hollow fibre was modified by grafting polyethylene glycol (PEG) with γ -ray irradiation to improve the ultrafiltration performance.

Keywords: Hollow-fibre membranes; Performance; Surface treatment; Spinning conditions

1. Introduction

Despite its usefulness and adaptability to different membrane separation processes [1–10], the fundamental study on the hollow fibre is very scarce in the literature. The reason may be that flat-sheet membranes are relatively easy to prepare, and the fundamental principles underlying membrane formation and membrane transport are considered to be the same regardless of the membrane shape and membrane configuration.

However, there are some differences between hollow-fibre and flat-sheet membranes. While hollow

fibres are mechanically self-supporting, flat-sheet membranes are usually cast on solid backing materials. During the solution spinning process, hollow fibres often require internal and external coagulants causing polymer gelation both on the bore and on the shell side of the hollow fibre. The internal stress by the swelling or shrinking of the polymer during solvent evaporation and solvent exchange in the gelation process is also different from that of flat-sheet membranes because of the circular shape of the hollow-fibre cross-section. Excessive stress can result in the formation of cracks on the hollow-fibre surface. The hollow-fibre geometry including the inner radius and the fibre thickness is governed by the hollow-fibre spinning conditions such as the spinneret geometry, coagulant flow-rate, poly-

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mer solution viscosity, polymer solution flow-rate and air gap. The fibre geometry affects the hydraulic pattern of the feed and permeate solutions, which in turn affects the mass transfer coefficient and the pressure drop in the hollow fibre. All these problems should be addressed and elaborated in the research concerning hollow-fibre membranes.

The effect of the internal coagulant on the pore size and the pore size distribution of the hollow-fibre membrane and the effect of the mass transfer on the bore side on the ultrafiltration performance were discussed by Liu et al. [11]. Previous study has shown that the spin solution composition, length of air gap and pressure used for fibre extrusion affect the fibre performance and fibre dimension [12].

The objective of this work is to investigate further in detail the effect of fibre spinning conditions on the fibre geometry. The effect of the spinning conditions on the ultrafiltration performance is also investigated. Another objective of the present work is to modify the surface on the bore side of the hollow fibre by grafting PEG with γ -ray irradiation. The purpose of the surface modification is to improve the ultrafiltration performance by increasing the hydrophilicity of the internal surface.

2. Experimental

2.1. Materials

Polyether sulfone 600P (PES), supplied by Imperial Chemical Industries, was used as membrane material. Polyvinylpyrrolidone (PVP) of molecular weight 10 000, supplied by Sigma, was used as the polymer additive to the spinning dope. N-Methyl-2-pyrrolidone (NMP), supplied by BDH, was used as the solvent. PEG of different molecular weights, supplied by Fluka, were used as the reference solutes to test hollow-fibre membrane performances.

2.2. Preparation of hollow fibres

Hollow fibres were made by the wet-dry spinning process. The spinning system was the same as that described in detail in Liu et al. [11] except there was no hollow-fibre take-up. Instead, the hollow fibre dropped freely under the gravitational effect into a coagulation bath (Fig. 1). Therefore, the flow velocity

of the polymer solution was governed primarily by that of the internal coagulant and the viscosity of the solution. The PVP/PES ratio in the casting solution was changed from 0.2 to 1.0, while the polymer PES content was kept constant at 22 wt.-%. In order to study the effect of spinning conditions, the parameters involved in the hollow-fibre spinning process were changed in the range summarized in Table 1.

Solutions of three components PES, PVP and NMP with various weight fractions were prepared as the spinning dope. The viscosity of a typical casting dope was 1.0 Pa s. The solution was then loaded into the reservoir heated to a predetermined temperature. The dope was forced to the spinneret by nitrogen pressure (extrusion pressure, P), which was varied depending on the viscosity of the casting dope under the condition of free extrusion, and was collected in a coagulant bath that was placed at an air gap, h , under the spinneret and kept

Fig. 1. Schematic diagram of hollow-fibre spinning system.

Table 1
Range of variation of parameters involved in hollow-fibre spinning

Parameter	Range of variation
Temperature of spinning dope, T ($^{\circ}\text{C}$)	25–60
Flow-rate of inner coagulant fluid, Q_w (ml/s)	6.0–30.6
Air gap, h (cm)	60
Polymer solution extrusion pressure, P (kPa)	34.5–206.9

Fig. 2. Spinneret nozzle geometry.

at 4°C. The volumetric flow-rate of the polymer solution was kept constant at 0.032 cm³/s by adjusting the valve A and the extrusion pressure P . The geometry of the spinneret is given in Fig. 2.

Some remarks are in order on the definition of Q_w , the volumetric flow-rate of internal coagulant determined experimentally without a concurrent flow of polymer solution (cm³/min), and u , the flow velocity of the internal coagulant with a concurrent flow of polymer solution (cm/min). The flow velocity of polymer solution should also be equal to u when a steady state is reached. The velocity u was not determined experimentally, however, u is expected to increase with an increase in Q_w .

2.3. Membrane surface modification

In order to improve the performance of hollow-fibre membranes, the internal skin layer of selected hollow fibres was treated with PEG polymers of various molecular weights. The hollow fibres were cut into the desired lengths immersed in water with nitrogen gas bubbled through it for 16 h. An aqueous solution of PEG in a syringe was deoxygenated by passing nitrogen gas through the solution. The deoxygenated polymer solution was then injected into the bore side of the fibre with a syringe against a stream of nitrogen gas. The fibres were drawn into wet glass tubes sealed with rubber stoppers, placed in a gamma cell for the appropriate times (0.5–2 h) and irradiated at a rate of 0.7

Mrad/h. After γ -ray irradiation, the hollow fibres were flushed with distilled water to remove excess polymer solution.

2.4. Morphology studies

In order to study the effects of spinning condition on the morphology of the hollow fibre, selected samples of hollow fibres were prepared for SEM investigation. Cross-sections of hollow-fibre membranes were prepared for SEM by quenching in liquid nitrogen and breaking the fibres at liquid nitrogen temperatures without damaging the fibres. The sample was then attached to a carbon holder and shadowed with a thin gold layer to prevent charging up of the surface by the electron beam. A narrow beam of electrons with kinetic energies in the order of 1–25 kV hits the membrane sample, and low-energy electrons were liberated from the atoms in the surface to create the image on the micrograph.

2.5. Ultrafiltration experiments

Hollow fibres were tested in bundles of one to three fibres, each 28 cm long. The fibres were potted at both ends with epoxy resin and mounted in a test module. The operating pressure and feed flow-rate were 20 p.s.i.g. and 1 m/s, respectively. The feed solution was supplied to the bore side of the hollow fibre, and the permeate was collected from the shell side. The PEG solute concentration in the feed solution was kept at 200 ppm. The concentrations of the feed and permeate solutions were determined by using a Beckman Model 915B carbon analyzer. The solute separation, f , was calculated by the following equation:

$$f = \frac{C_{\text{feed}} - C_{\text{permeate}}}{C_{\text{feed}}} \quad (1)$$

The pure water permeation rate, PWP, and the product rate for each solute, PR, were also obtained.

3. Results and discussion

3.1. Effect of the spinning conditions on the fibre geometry

Table 2 shows the change of λ_o , ratio of the outer radius (r_o) to the inner radius (r_i) of the hollow fibre,

Table 2

Ratio of outer radius to inner radius, λ_o , of hollow fibres spun at different flow-rates of internal coagulant

Membrane type	Q_w (cm ³ /min)	λ_o
R0.2-25	6.0	2.55
R0.2-25	30.6	1.28
R0.2-60	6.0	2.00
R0.2-60	30.6	1.25

Table 3

Change in dimension of hollow fibres spun from dopes at different temperatures

Membrane type	λ_o	r_i (cm)	Wall thickness (mm)
R0.6-45	1.33	0.045	0.150
R0.6-35	1.35	0.050	0.175
R0.6-25	1.61	0.045	0.275

Table 4

Effect of PVP weight fraction in the dopes on dimensions of hollow fibres

Membrane type	λ_o	r_i (cm)	Wall thickness (mm)
R0.2-25	2.55	0.0255	0.395
R0.6-25	1.61	0.0450	0.275
R0.8-25	1.67	0.0450	0.300
R1.0-25	1.36	0.0625	0.225

with an increase in the flow-rate of the inner coagulation fluid, Q_w . A code was given to each membrane according to the casting solution composition and casting solution temperature. For example, the code R0.2-25 means that the PVP/PES ratio in the casting solution was 0.2, and the casting solution temperature was 25°C. The same system of the membrane code will be used in Tables 2–5.

As discussed in the experimental section, the average flow velocity of the polymer solution, u , is supposed to increase with increasing Q_w . Remember that the volumetric flow-rate of the polymer solution, V , was kept constant throughout the experiments. Then, λ_o should decrease with increasing Q_w , since the following equation holds:

$$V = \pi r_i^2 (\lambda_o - 1)^2 u \quad (2)$$

The data in Table 2 meet the above expectation.

Table 3 shows that λ_o and wall thickness increased with decreasing casting solution temperature. The

PVP/PES ratio was kept constant at 0.6 for this series of experiments. These results can also be easily explained by Eq. 2. Since the viscosity of the casting solution increases with decreasing temperature (see Appendix), u should decrease. Then, λ_o increases to maintain V constant.

Finally, Table 4 shows that, at a constant casting solution temperature, the increase in PVP/PES ratio results in a decrease of λ_o ($= r_o/r_i$). This, at a first glance, looks strange, since an increase in PVP/PES ratio also causes an increase of solution viscosity μ (see Appendix) and consequently a decrease of u . However, Table 4 shows also that the inner radius of the hollow fibre, r_i , increases significantly with an increase in PVP/PES ratio. Examining closely r_i values, the latter is almost the same as the radius of the nozzle outlet for the internal coagulant (0.025 cm), when the PVP/PES ratio is 0.2. The r_i value increases and becomes exactly the same as the inner radius of the casting solution nozzle at PVP/PES ratios of 0.6 and 0.8, and even larger at a PVP/PES ratio of 1.0. This indicates that the casting solution is drawn to the internal coagulant stream of high velocity when the polymer solution viscosity is low. At higher viscosity this effect should be much less pronounced. At the highest PVP/PES ratio of 1.0, r_i was even greater than the inner radius of the polymer solution nozzle. Although the reason is not clear, the contraction of the polymer solution volume as a result of the solvent-coagulant exchange may be one of the reasons.

Therefore, there are two opposing effects of increasing PVP/PES ratio on the λ_o value. One is the effect of increasing viscosity, which decreases u and λ_o according to Eq. 2. The other is the effect of increasing r_i value, which results in a decrease in λ_o according to Eq. 2. Obviously, the latter effect overcompensated the former effect when the PVP/PES ratio was increased.

3.2. Effects of the composition of the casting solution and its temperature on the ultrafiltration performance

The effect of the casting composition and the casting solution temperature on the ultrafiltration performance was investigated by measuring the separation of PEG solutes of various molecular weights and the permeation rate. The results are listed in Table 5. Some of the selected results are illustrated in Fig. 3. Since the concentration of the PEG solute in the feed solution was

Table 5
Performance data of PES hollow-fibre membranes

Membrane type	PWP (g/cm ² h)	PEG 1500 Solute separation, <i>f</i> (%)	PEG 3000	PEG 6000	PEG 9000
R0.2-25	4.03	23.64	56.76	84.40	95.09
R0.2-35	7.87	43.23	73.41	88.23	95.43
R0.2-45	5.25	62.96	73.87	82.18	91.87
R0.2-60	7.53	44.10	69.50	84.18	88.51
R0.4-25	3.11	70.13	83.84	92.18	95.11
R0.4-35	7.58	59.54	72.50	82.06	95.29
R0.4-45	7.41	31.85	60.21	79.16	92.99
R0.4-60	9.95	47.28	64.56	76.84	86.88
R0.6-25	4.06	52.37	74.92	87.14	92.53
R0.6-35	13.53	39.04	66.92	85.85	88.11
R0.6-45	20.43	21.95	47.28	67.92	80.70
R0.6-60	21.61	23.78	40.20	60.16	69.54
R0.8-25	7.08	29.59	63.67	80.76	87.65
R0.8-35	9.21	32.76	64.86	82.60	87.77
R0.8-60	5.39	30.71	44.45	75.15	87.38
R1.0-25	15.58	25.09	43.34	66.91	86.14
R1.0-45	17.77	21.79	37.57	66.50	87.51
R1.0-60	19.13	24.33	42.06	66.27	87.51

small (200 ppm), the osmotic pressure effect was almost negligible. Therefore, the permeation rate with and without the presence of the solute in the feed were practically equal. Therefore, only the pure water permeation flux is reported in Table 5. Further, the velocity of the feed flow in the bore of the hollow fibre was 1 m/s. According to the evaluation of the mass transfer coefficient in the previous work with hollow fibres whose geometry was similar to the present ones, the mass transfer coefficient corresponding to the above feed velocity is $5.6 \cdot 10^{-6}$ m/s for PEG 1500 solute. For this value of the mass transfer coefficient and the permeation velocity of the solution, the concentration polarization effect is not necessarily negligible. Care must be taken, therefore, to interpret the experimental data.

When we look at the data at 25°C in Table 5, a maximum solute separation is found at a PVP/PES ratio of 0.4, while an increasing tendency is observed in the pure water permeation flux with an increase in the PVP/PES ratio. The decreasing tendency of the solute separation observed at the high PVP/PES ratios could be the result of concentration polarization. These results are in accordance with the work of Lafrenière et al. [13], in which they found that the flux showed a maximum when the PVP/PES ratio was 1.0. Since their work was performed with flat membranes with a back-

Fig. 3. Effect of temperature of casting solution on performance and geometry of hollow fibres spun with different weight ratios of additive: (□) PVP/PES = 0.6, (●) PVP/PES = 1.0.

Table 6

Comparison of performance of hollow fibres with various surface modification conditions

Membrane type ^a	PWP (g/cm ² h)	PEG 1500 Solute separation, <i>f</i> (%)	PEG 3000	PEG 6000	PEG 9000
S-NC	6.04	71.26	90.08	97.75	98.72
S-10K-1	4.67	55.49	75.63	90.77	94.64
S-35K-1/2	4.29	59.05	81.56	90.92	93.80
S-35K-1	4.70	63.85	81.56	90.44	94.70
S-35K-2	5.17	66.70	85.09	94.09	94.48
S-100K-1	6.75	69.72	86.57	95.59	96.20

^aAll hollow fibres are prepared from PES polymer (Vitrex 200P) solution (22 wt.-%) in dimethylacetamide solvent with a PVP/PES ratio of 0.4. The casting temperature was 25°C.

ing support material and the present work with hollow-fibre membranes, the above agreement indicates that at least the effect of the PVP/PES ratio on the membrane performance is common for both flat-sheet and hollow-fibre membranes. They also concluded from the intrinsic viscosity measurement that the interaction between the PVP and PES polymers is strongest when the PVP/PES weight ratio is in the range 0.4–1.0. It should also be noted that the permeation rate of flat-sheet membranes in the work of Lafrenière et al. [13] is in the same range as that of the hollow fibre membranes developed in the present work.

The effect of the casting solution temperature on the membrane performance is depicted in Fig. 3, where the separation of the PEG solute with a molecular weight of 6000 and the pure water permeation flux (PWP) are illustrated versus the casting solution temperature together with the hollow-fibre wall thickness. While solute separation, pure water permeation flux and wall thickness are practically constant with respect to a PVP/PES ratio of 1.0, solute separation decreases, pure water permeation flux increases and wall thickness decreases with increasing casting solution temperature

with respect to a PVP/PES ratio of 0.6. This data indicates that the effect of the casting solution temperature on the membrane geometry and the membrane performance is small when the PVP content in the casting solution is large, and consequently the viscosity of the casting solution is high.

It has been shown above that the pure water permeation flux is closely related to the wall thickness. This correlation, however, should not be overemphasized. It is known that the flux of the asymmetric membrane is governed by the thickness of the active surface layer and not by the total membrane thickness. The correlation between the pure water permeation flux and the total membrane thickness can only be expected when the thickness of the active surface layer increases when the total membrane thickness increases, or vice versa.

3.3. Effect of PEG grafting by γ -ray irradiation

Tables 6–9 summarize the results of the experiments for hollow fibres whose inner surface was modified by grafting PEG by γ -ray irradiation. The molecular weight of PEG, the duration of γ -ray irradiation and

Table 7

Comparison of performance of hollow fibres with various surface modification conditions

Membrane type	PWP (g/cm ² h)	PEG 1500 Solute separation, <i>f</i> (%)	PEG3000	PEG6000	PEG 9000
R0.2-35-NC	7.87	43.23	73.41	88.23	95.43
R0.2-35-10K1	1.98	24.68	57.60	83.38	94.62
R0.2-35-35K1/2	4.56	23.64	59.90	84.26	94.93
R0.2-35-35K1	2.36	23.71	58.29	84.11	93.93
R0.2-35-35K2	0.28	22.34	52.74	83.47	86.11
R0.2-35-100K1	3.87	38.28	67.13	85.95	94.66

Table 8

Comparison of performance of hollow fibres with various surface modification conditions

Membrane type	PWP (g/cm ² h)	PEG 1500 Solute separation, <i>f</i> (%)	PEG 3000	PEG 6000	PEG 9000
R0.6-45-NC	20.43	21.95	47.28	67.92	80.72
R0.6-45-10K1	24.05	14.87	30.74	54.33	72.42
R0.6-45-35K1/2	28.54	16.85	32.88	43.59	68.43
R0.6-45-35K1	26.26	16.84	28.51	44.00	72.98
R0.6-45-35K2	19.52	16.50	27.93	46.18	76.38
R0.6-45-100K1	17.96	25.84	47.30	63.26	83.24

the pore size of PES membranes before the surface treatment, which are called PES base membranes hereafter, are the three variables involved in this work. Codes are given to each membrane listed in Tables 6–9. For example, R0.2-35-NC indicates that the base PES membrane is the same as R0.2-35 in Table 5 and the membrane was subjected to no surface modification. R0.2-35-10K-1 means that the base PES membrane is R0.2-35 and the inner surface of the hollow-fibre membrane was treated with PEG of molecular weight 10 000 and the duration of γ -ray irradiation was 1 h. There are two base membranes that are not included in Table 5. Codes S and T are given to those base membranes for which the conditions of membrane preparation are given in detail in the footnotes of Tables 6–9.

With respect to the results of the first three groups of data including those for S, R0.2-35 and R0.6-45 base membranes (Tables 6–8), the solute separation is either unchanged or lowered with the surface treatment. Only in the case of the R0.6-45 base membrane, a slight increase is observed when the membrane surface was modified with PEG of molecular weight 100 000 and the duration of γ -ray irradiation was 1 h. Since the

solute separation of R0.6-45-NC is lower than those of S-NC and R0.2-35-NC base membranes, a more spectacular effect of the surface modification would be expected when the pore size of the base membrane would be even larger. A PES base hollow-fibre membrane was prepared, therefore, from a polymer solution without any PVP additive. It is known from the experiment with flat-sheet membranes that the pore size becomes larger (consequently solute separation becomes smaller) and flux becomes significantly lower when a membrane is cast from a casting solution without any PVP additive.

Referring to the data in Table 9, the same effect is observed with respect to hollow-fibre membranes, i.e. both separation and pure water permeation flux decrease significantly compared with membranes cast from the casting solutions including PVP. The data in Table 9 also show that the solute separation increases progressively with an increase of the molecular weight of the grafted PEG from 10 000 to 200 000 with some sacrifices in the pure water permeation flux. The concentration polarization effect is negligible when the pure water permeation flux, PWP, is below 1 g/cm² h. Therefore, the results in Table 9 reflect the real effect

Table 9

Comparison of performance of hollow fibres with various surface modification conditions

Membrane type ^a	PWP (g/cm ² h)	PEG 1500 Solute separation, <i>f</i> (%)	PEG 3000	PEG 6000	PEG 9000
T-NC	1.02	13.60	9.37	21.25	74.38
T-10K-1	0.40	31.20	54.82	64.29	96.32
T-35K-1	0.37	36.30	59.54	80.14	93.39
T-100K-1	0.63	40.63	59.36	82.61	96.80
T-200K-1	0.62	54.90	74.90	86.60	96.94

^a All hollow fibres are prepared from PES polymer (Vitrex 600P) solution (25 wt.-%) in NMP solvent without any PVP. The casting temperature was 25°C.

Fig. 4. Comparison of finger-like cavity structure of hollow fibres spun from casting solution with different weight ratios of additives at 45°C: (a) PVP/PES=0.2, (b) PVP/PES=0.4 and (c) PVP/PES=1.0

of PEG grafting. These data indicate that the pore size of the base membrane should be sufficiently large for the surface modification to be effective.

3.4. Electron micrographic observation

Fig. 4 shows the electron micrographic picture of the cross-sections of hollow-fibre membranes R0.2-45 (a), R0.4-45 (b) and R1.0-45 (c), respectively. Fig. 4a clearly indicates the presence of two dense layers both on the bore side and on the shell side of the hollow fibre, large finger-like voids being sandwiches in between. Finger-like macrovoids appeared even when PVP was added. The macrovoid may disappear when the molecular weight of PVP is higher than 10 000 [14]. It is also interesting to note that there is a boundary between the region of small finger-like voids and that of large finger-like voids near the shell side surface of the hollow fibre. This is considered to be the boundary where the flows of the gelation media by diffusion from the bore side and from the shell side meet. Fig. 4b and c indicate that more space is occupied by the finger-like voids and the front of the finger advances more towards the shell side surface when the PVP content in the casting solution is higher. This can be attributed to the hydrophilic nature of the PVP additive, which, at higher PVP/PES ratios, draws a larger amount of water into the polymer solution before it enters the gelation bath. Fig. 4c also shows that the inner dense layer is much thicker, which indicates that the gelation takes place as soon as the casting solution leaves the nozzle of the spinneret.

4. Conclusions

From the above experimental results and theoretical considerations, the following conclusions can be drawn:

Under the condition of a constant flow-rate of the polymer solution and a constant inner radius of the hollow fibre:

- 1) The ratio (outer radius/inner radius) of the hollow fibre decreases with an increase in the flow-rate of the internal coagulant.
- 2) The above ratio decreases with an increase in the casting solution temperature.

Under the condition of a constant flow-rate of the polymer solution:

- 3) The above ratio decreases with an increase in the inner radius of the hollow fibre.
- 4) The above ratio decreases with an increase in the viscosity of the polymer solution, since the inner radius of the hollow fibre increases together with the solution viscosity.

As for the ultrafiltration performance of hollow-fibre membranes:

- 5) The separation of PEG solutes and the membrane flux are functions of PVP/PES ratio in the polymer solution and the polymer solution temperature.
- 6) The separation of PEG solutes increases significantly by grafting PEG to the internal surface of the hollow fibre by γ -ray irradiation. However, the

separation of PEG 6000 by the base hollow fibre should be as low as 20% under the ultrafiltration conditions with an operating pressure of 20 p.s.i.g. and a feed concentration of 200 ppm for the grafting to be effective.

- 7) Since the hydrophilicity of the internal surface of hollow fibres is increased by PEG grafting, the hollow fibre becomes less susceptible to fouling by the adsorption of organic contaminants. Therefore, the surface-modified hollow fibres have great advantage in practical applications.

Electron micrographic pictures of the cross-section of the hollow fibre revealed that the proportion of the finger-like void space increases when a larger quantity of PVP is added to the polymer solution.

Figure A.2 Effect of Temperature on Solution's Viscosity

Fig. A1 + A2. Effect on PVP/PES ratio on solutions viscosity.

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Appendix 1

Table A.1
Composition of PES solutions

Solution No.	PVP (wt.-%)	PES (wt.-%)	NMP (wt.-%)	PVP/PES ratio
1	4.4	22.0	73.6	0.2
2	13.2	22.0	64.8	0.6
3	17.6	22.0	60.4	0.8
4	22.0	22.0	56.0	1.0

Table A.2
Effect of temperature and composition on the viscosity of PES solutions

Solution No.	Solution viscosity (Ps s)		
	Solution temperature		
	26°C	40°C	60°C
1	57.8	37.2	22.4
2	334.6	176.4	81.2
3	520.0		
4	1266.0		

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