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EFFECT OF RHEOLOGICAL BEHAVIOUR OF CELLULOSE ACETATE SPINNING SOLUTIONS ON PERFORMANCE OF REVERSE OSMOSIS HOLLOW FIBER MEMBRANES

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Abstract. Rheological assessment of cellulose acetate spinning solution using a rotational rheometer and an optical shear cell is carried out so as to study the cause and effect relationship between membrane preparation, polymer morphology and membrane performance. The power law bahaviour, normal force and flow profiles generated provided clues regarding phase inversion and molecular orientation. These rheological results are then related to the separation performance of cellulose acetate reverse osmosis (RO) hollow fibers membranes; both the rejection rate and the flux rate increased with increasing dope extrusion rate, possibly due to molecular orientation.

Key words: spinning rheology; reverse osmosis; hollow fiber; molecular orientation

Abstrak. Kajian ini bertujuan untuk menyelidik kesan reologi semperitan terhadap membran gentian geronggang osmosis balikan. Ini dilakukan dengan penilaian reologi larutan semperitan selulosa asetat menggunakan sebuah reometer putaran dan sel optik ricih. Sifat hukum kuasa, daya normal dan profil aliran yang terjana memberi penjelasan mengenai fasa balikan dan orientasi molekul. Keputusan reologi ini kemudiannya dihubungkaitkan dengan prestasi membran gentian geronggang osmosis balikan dari segi kadar buangan and kadar fluks. Keputusan kajian menunjukkan bahawa kadar buangan dan kadar fluks meningkat apabila kadar semperitan larutan meningkat dan ini mungkin disebabkan oleh orientasi molekul.

Kata kunci: reologi semperitan; osmosis balikan; gentian geronggang; orientasi molekul

1.0 INTRODUCTION

The properties of membranes are known to be dependent on many factors amongst which are phase inversion parameters and rheological conditions [1]. Phase inversion governs the general morphology of the fiber whereas rheological properties under shear and elongation further effect chain conformation, i.e. orientation in the skin layer. Therefore, these twin effects of phase separation and rheology (shear and elongation) determine the properties of the final product.

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Besides phase inversion conditions and thermodynamic studies which have always been the focus of most membrane studies, rheologically induced molecular orientation is another aspect of membrane development that has only recently been considered by membranologist if membrane performance is to be heightened beyond the recognised intrinsic value of the particular polymer. This aspect has been recently proven for gas separation [2,3].

In a recent study [4,5], both the phase inversion and rheology factors were systematically studied for RO membranes. Since the spinning of hollow fiber membranes involved many factors, including both the phase inversion and the rheological factors, a systematic approach was taken to study some of these main factors. The Taguchi method, a powerful tool for design optimization [6–9] has been used as a screening tool to determine the significant factors affecting the spinning process and the optimal spinning parameters. It involves the use of an orthogonal array, the signal-to-noise ratio (S/N) ratio and the analysis of variance (ANOVA) to study these spinning process factors. The spinning process factors studied and their levels are given in Table 1. The detailed results of the above will be reported elsewhere [4,5]. However as a summary, the study revealed the bore fluid (BF) and dope extrusion rate (DER) exert the most significant effect on the percent rejection rate.

Table 1 Spinning process factors and their levels

	Factors	Levels	
		1	2
A	Polymer content (%) (PC)	25	27
B	Acetone/formamide ratio (A/R)	1	1.5
C	Bore Fluid type (BF)	0.9	1.0
D	Dope extrusion rate (ml/min) (DER)	2.5	4
E	Residence time (sec) (RT)	0.266	0.615
F	Gas flushing rate (l/min) (GR)	2	4

The bore fluid contributes to 61% of the variation in the experiment whereas the dope extrusion rate contributes to 12% of the variation. Other factors such as polymer content (PC), gas flushing rates (GR) and residence time (RT) contribute to the rest of the variation. The order of importance of the factors that influenced the rejection rate are BF > DER > PC > GR > RT. The acetone to formamide (A/F) ratio factor is insignificant and thus omitted.

The optimum settings, levels and percent contribution of the various factors are given in Table 2 and at these optimum settings, the expected response, which is the rejection rate, is found to be 95.7%. A confirmation run was carried out where hollow

Table 2 Optimum spinning conditions and percent contribution of significant factors

	Factors	Level Description	Level	% Contribution
A	PC (%)	27	2	6.5
B	A/F Ratio	–	–	0
C	BF	1	2	61.0
D	DER (ml/min)	4	2	12. 3
E	RT (sec)	0.615	2	2.1
F	GR (l/min)	4	1	5.6

Table 3 Rejection rate results of confirmation run experiment

Sample No.	% Rejection rate
1	95.5
2	95.8
3	94.2
Average	95.2

fiber membranes were spun at the optimum settings and tested. The results of the confirmation run are shown in Table 3. The average response for the confirmation run, which is repeated three times, is found to be 95.2 % and this value is well within the limits of the confidence intervals of the expected response (± 6.0 at 95% confidence limit).

As mentioned previously, the bore fluid (BF) and dope extrusion rate (DER) exert the most significant effect on the percent rejection rate and this is followed by polymer content. Unlike bore fluid [10,11], which has been the subject of some previous fundamental phase inversion work, rheological factors, such as dope extrusion rate, have not been treated in any detail for RO hollow fiber membranes.

Recently, the polysulfone solution used to produce enhanced selectivity gas separation hollow fiber membranes was rheologically assessed using rotational rheometer and an optical shear cell [12]. It is believed that such rheological knowledge is useful if membrane structure and performance are to be related to the flow conditions experienced in the spinneret. In view of this, it is therefore crucial to determine the rheological properties of cellulose acetate polymer solution experimentally so as to understand how they influence the morphology and separation performance of membrane, subsequently explaining for the results of rheological factors in Table 2.

2.0 EXPERIMENTAL

2.1 Preparation of the Polymer Spinning (dope) Solution

The concentrated cellulose acetate dope solution that were employed in the spinning of the reverse osmosis hollow fiber membranes in Taguchi experimental design study were subjected to rheological characterisation under shear using a rotational rheometer and an optical shear cell. Four different dope-spinning solutions were used in the spinning of RO hollow fibers in the Taguchi experimental design study:

(i) Cellulose acetate 25%, acetone 37.5% and formamide 37.5% (ratio =1)
(ii) Cellulose acetate 25%, acetone 45% and formamide 30% (ratio = 1.5)
(iii) Cellulose acetate 27%, acetone 36.5% and formamide 36.5% (ratio = 1)
(iv) Cellulose acetate 27%, acetone 43.8% and formamide 29.2% (ratio = 1.5)

Cellulose acetate of concentration 25 and 27wt % (Aldrich Chemicals, 39.8% acetyl content, average molecular weight 30 000) was dissolved in mixtures of acetone (solvent) and formamide (nonsolvent) of two different ratios (1 and 1.5) as listed above. The polymerization temperature was maintained in the region of 50°C and a high stirrer was maintained so as to assist the dissolution of polymers. After the polymer was fully dissolved, the polymer was cooled, poured into a storage bottle and degassed to remove any micro bubbles present.

2.2 Rheometer

The rheological tests were measured using the TA instruments AR 1000 Rotational Rheometer. Reliable and consistent results were achieved using the 2 cm parallel plate geometry with test duration of 5 min. The standard gap size for the tests was 100 mm and a 20 s period of pre-shear at a minimum shear rate was employed at the start of each test. In order to prevent the evaporation of the highly volatile solvent, acetone, from the rim, it is essential to shroud the geometry with a solvent trap. A ring of dope is deposited within the solvent trap so as to equilibrate the sample with the local environment. Under such conditions, the continuous ramped experiment was used to study the flow behavior of the dope solution. Each flow curve was obtained as an average of at least 6 measurements.

2.3 Optical Shear Cell

In order to visually observe the dope behavior under shear, an optical shear cell was used. The sample was placed between two parallel glass discs of diameter 4.0 cm. The bottom glass disc was attached to a driving gear and was rotated by a variable speed motor while the upper disc was fixed. The precision spacers that were placed between the upper and lower stainless housings determined the gap height. The sample

was illuminated by scattered white light from below and observed from above. For parallel plate measurements, the shear rate $\dot{\gamma}$ is a linear function of the sample radius, r given by

$$\dot{\gamma} = \omega r d \tag{1}$$

where d is the gap height (m) and ω is the angular velocity (rad/s). The shear rate is at a maximum at the outer edge of the sample and decreases to zero in the center. In this study three gaps of 250, 500 and 750 mm and a maximum speed of about 83.7 rad/s were used providing a maximum shear rate achievable of about 1466 s^{-1}. These experiments accurately reflect those experienced in the rheometer.

3.0 RESULTS AND DISCUSSION

3.1 Flow Curves at 25°C

The viscosities (η) and normal forces exerted by the various dopes as functions of shear rate (γ) measured at 25°C are shown in Figures 1 to 4. These are output from the Rotational Rheometer. Each curve shown is an average of 6 curves. Four distinct regions (I–IV) of behavior can be detected. At very low shear rates (region I, below approximately 1 s^{-1}) fluctuations and non-linear data are observed for all the dope solutions due to limitations in equi pment precision. However it can be seen that in region II, the dope behaves like a Newtonian fluid, where the viscosity of each dope solution is almost constant. This is very clearly seen for dope solution containing 25%

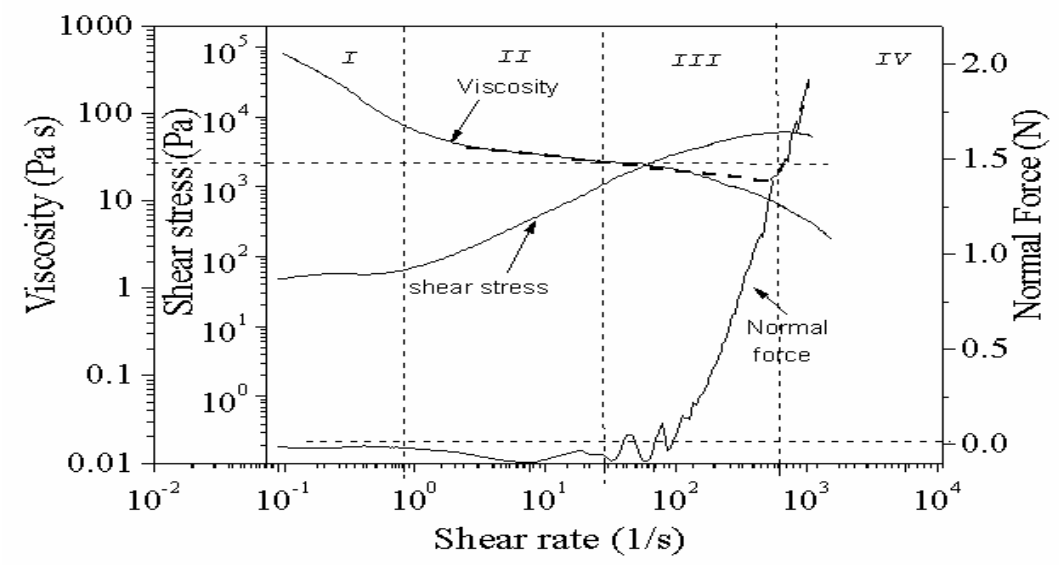

Figure 1 Flow curve with normal force at 25°C for 25% CA, 37.5% acetone and 37.5% formamide (Ratio of acetone to formamide = 1)

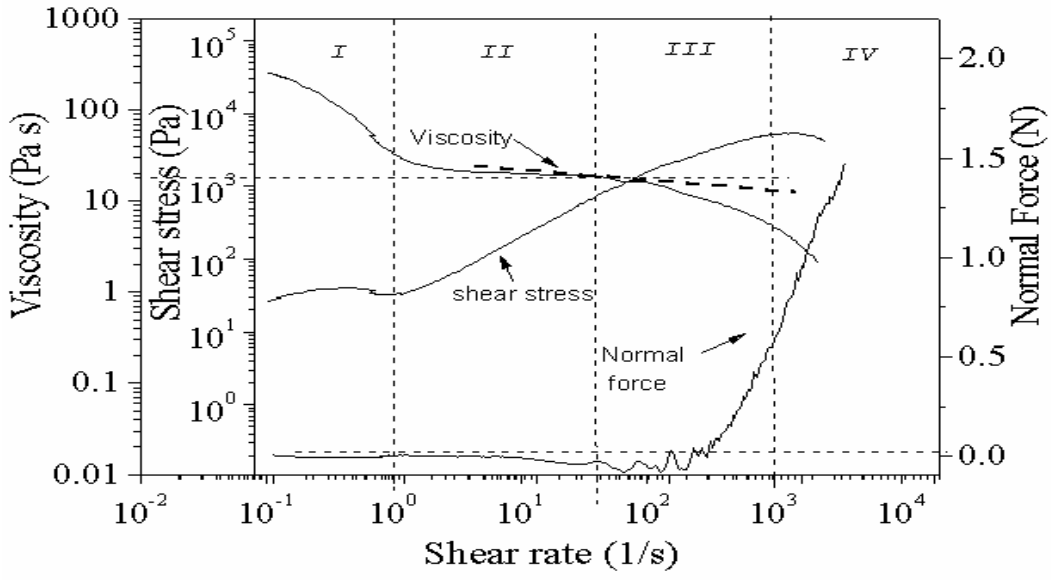

Figure 2 Flow curve with normal force at 25°C for 25%CA, 45% acetone and and 30% formamide (Ratio of acetone to formamide = 1.5)

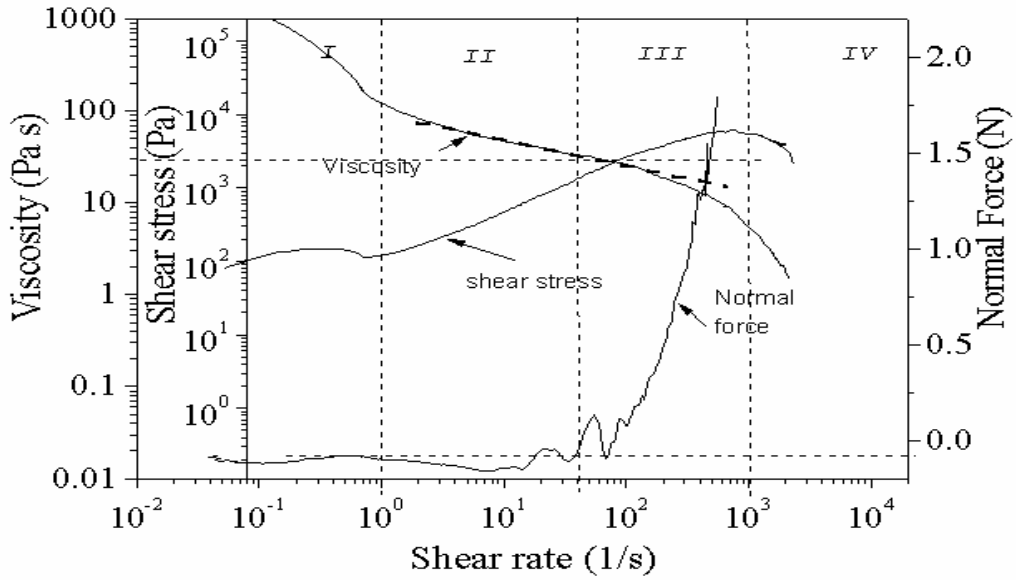

Figure 3 Flow curve with normal force at 25°C for 27%CA, 36.5% acetone and 36.5% formamide (Ratio of acetone to formamide =1)

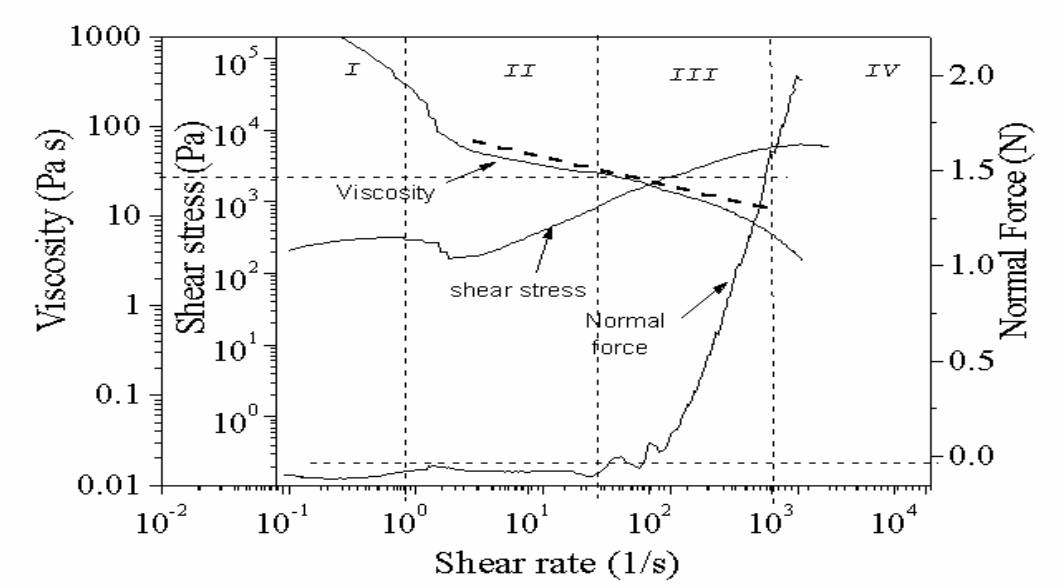

Figure 4 Flow curve with normal force at 25°C for 27%CA, 43.8% acetone and 29.2% formamide (Ratio of acetone to formamide = 1.5)

Table 4 Spinning dope behavior under shear

Dope	Power Law Index, *n*	Constant, *k*
25% Cellulose Acetate, 45% Acetone and 30% Formamide	0.55	125.32
25% Cellulose Acetate, 37.5% Acetone and 37.5% Formamide	0.48	274.85
27% Cellulose Acetate, 43.8% Acetone and 29.2% Formamide	0.48	267.65
27% Cellulose Acetate, 36.5% Acetone and 36.5% Formamide	0.40	495.85

CA, 45% acetone and 30% formamide. No normal force is detected in this region. However observation of this region becomes difficult when the concentration of polymer is increased to 27% and the amount of solvent, acetone, is reduced. In spite of this, when shear rates get higher, the presence of a normal force is detected and this is observed for all the dopes. This is designated as the first critical shear rate and material starts to exhibit deviation from linear viscoelastic response. (Region III). Thus, all the dopes displayed classical shear thinning power law properties. A power law given by

$$\eta = k\dot{\gamma}^{n-1} \tag{2}$$

where k is a measure of the consistency of the fluid and n is a degree of non-Newtonian behavior, fits well with the flow curve in this region. These power law indices n and constants k for the spinning dopes are deduced from these flow curves and are tabulated in Table 4. The power law relates to the thickness of the dope where the higher the k value, the higher is the apparent viscosity, whereas the power law index relates to the shear thinning behavior where the lower the n value the greater the shear thinning and molecular alignment. The k values for 27% CA dope solutions are much higher compared to dope solutions containing 25% CA indicating an increase in viscosity, however the n values are much lower indicating shear thinning behavior and greater molecular alignment.

However there exists a further gradient change, termed the second critical shear rate (SCSR) at even higher shear rates beyond which viscosity decreases rapidly with increasing shear rate (Region IV). This effect is observed with rotational rheometers at high rotational speed and is associated with the sample loss induced by high centrfugal forces. The results obtained are in line with work done by Gordeyev, *et al.* [12] on polysulfone polymers.

3.2 Optical Shear Cell

Room temperature tests were performed at various rotational speeds and gap setting. (The speed was increased in steps at each gap settings). During these experiments, the fragments of the fluid sample were thrown out of the apparatus resulting in a decrease in the diameter of the sample. After about 45 to 50 seconds, a constant sample size diameter was obtained and this loss in sample was attributed to centrifugal force, F where

$$F \propto \omega^2 r \tag{3}$$

After each rotational speed, ω, the radius of the sample, r, remaining in the cell was measured so as to determine the centrifugal force that could be withstand by the dope and also the shear rate experienced. These results were then tabulated in Table 5. A graph of shear rate versus gap size is then plotted and shown in Figure 5. Inspite of the difficulty in interpreting the data, the dope seemed to experience different strength. The fluid was able to withstand greater centrifugal force at higher shear rates as the gap setting decreased: for a 750 μm gap, strength regime is formed at around 172 s^{-1} and could withstand forces of up to 5 N/kg whereas for the 250 μm gap, the structure formed at around 1195 s^{-1} and could withstand forces up to 16 N/kg. It could also be seen that the resistance to centrifugal force was much greater when gap settings are reduced.

Table 5 Optical cell data

Gap Height (μm)	Shear (s^{-1})	Centrifugal force (N/kg)	Gap Height (μm)	Shear (s^{-1})	Centrifugal force (N/kg)	Gap Height (μm)	Shear (s^{-1})	Centrifugal force (N/kg)
250	1536	8	500	628	7	750	256	2
250	1361	11	500	785	12	750	302	5
250	1256	13	500	837	17	750	188	4
250	1221	16	500	698	18	750	148	5
250	1214	19	500	628	20	750	128	5
250	1026	19	500	537	20	750	111	5
250	1005	21	500	558	23	750	114	6
250	943	22				750	130	8
Av	1195	16	Av	667	17	Av	172	5

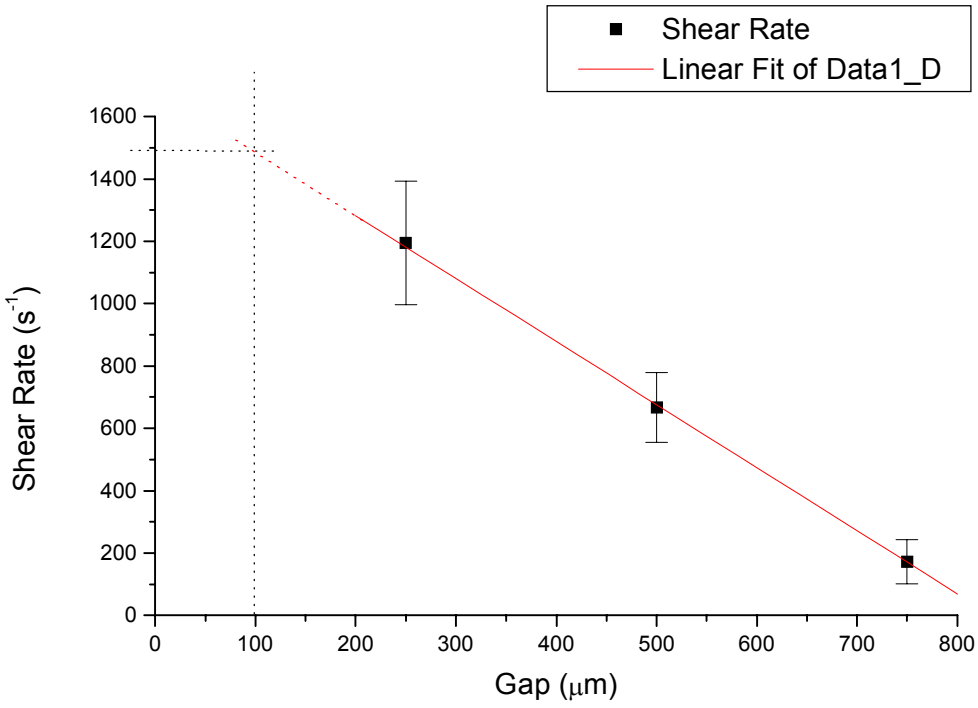

Figure 5 Shear rate versus gap size at sample boundary (optical shear cell data)

In general, it could be seen that as the gap setting decreases, the resistance of the dope to centrifugal force increases and this resistance occurs at higher shear rates and this can be seen from Figure 5. Thus results from the TA Instruments were very consistent and reliable since the standard gap size was set at 100 μm. Throughout the shear cell tests, no meaningful visible changes in sample transparency were noticed through out the shear cell test.

3.3 Establishment of the Flow Profile in the Spinneret during Hollow Fiber Membrane Spinning

Upon obtaining the values of k and n of the various dope solutions, the flow profiles experienced in the spinneret during hollow fiber spinning are established. The flow equations for the power law fluid passing through a concentric annulus in axial flow were derived by Shilton [13]. The equations are then solved for the power law index (k) and constant (n) of the various dope solutions to yield pressure drop, velocity profile, shear stress profile and shear rate profile induced during spinning. This kind of rheological knowledge is useful if membrane structure and properties are to be related to the flow conditions experienced in the spinneret.

The flow profiles data were generated for the various CA dope solutions using a program called 'Extrudate' [13,14]. The computer program employs a trial and error solution involving numerical analysis. The data generated from this program are used to plot the shear rate profiles experienced in the spinneret for the different dope rate extrusions shown in Figures 6 to 9.

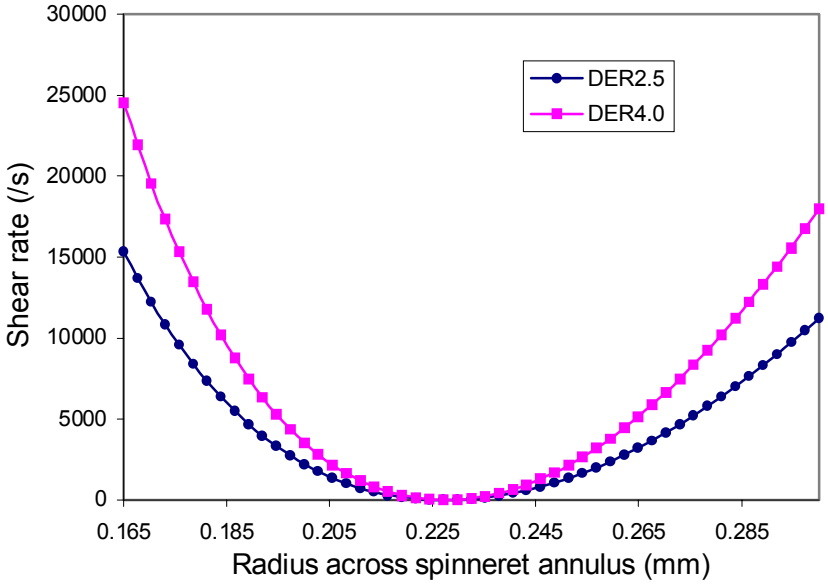

Figure 6 Shear rate profiles in spinneret at low and high dope extrusion rates with dope solution: 25% CA, 37.5% acetone and 37.5% formamide (ratio of acetone to formamide = 1.0)

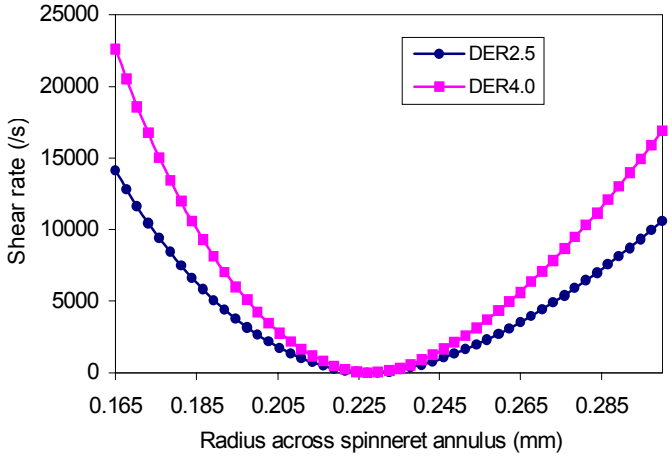

Figure 7 Shear rate profiles in spinneret at low and high dope extrusion rates with dope solution: 25% CA, 45% acetone and 30% formamide (ratio of acetone to formamide = 1.5)

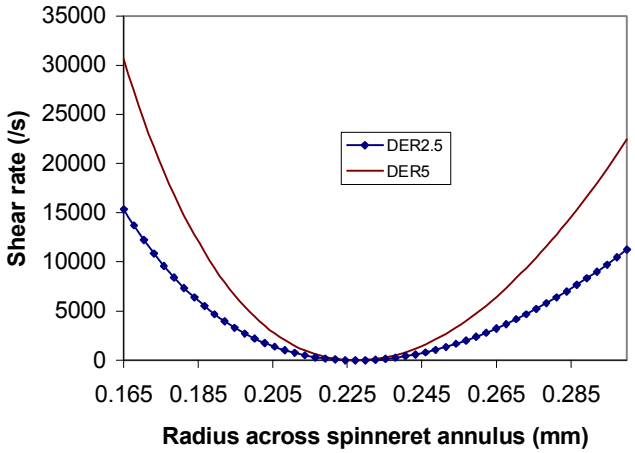

Figure 8 Shear rate profiles in spinneret at the various dope extrusion rates for dope solution: 27% CA, 36.5% acetone and 36.5% formamide (ratio of acetone to formamide = 1.0)

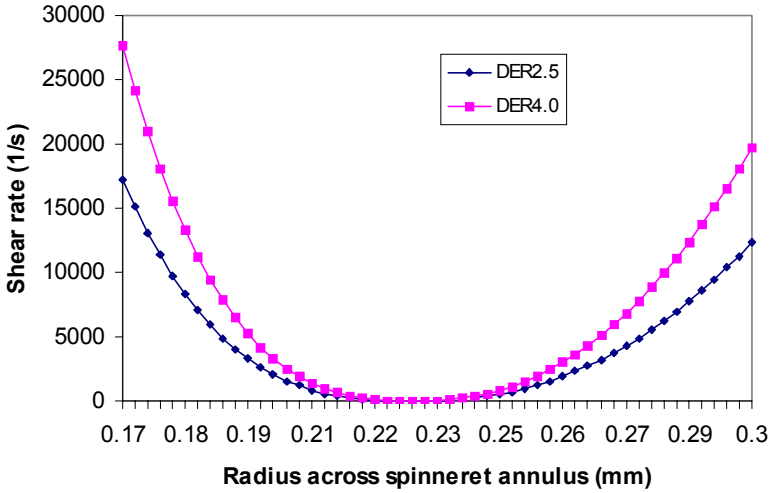

Figure 9 Shear rate profiles in spinneret at the various dope extrusion rates for dope solution: 27% CA, 43.8% acetone and 29.2 % formamide (ratio of acetone to formamide = 1.5)

Table 6 summarises the levels of shear experienced at the outer spinneret wall during hollow fiber spinning for the various dope solutions. It can be seen that with 25% CA, 37.5% acetone and 37.5% formamide, the levels of shear experienced at the spinneret wall during hollow fiber spinning are considerable: 11239 s^{-1} and 17982 s^{-1} for low and high dope extrusion rates of 2.5 and 4.0 ml/min respectively. When the ratio of the acetone to formamide is increased to 1.5 (45% acetone and 30% formamide), the shear rates at the spinneret decreases to 10582 s^{-1} and 16931 s^{-1} for low and high extrusions respectively. Therefore, the increase in the ratio of the acetone to formamide does not cause an increase in the shear rates experienced at the spinneret walls. However, when the CA content was increased to 27%, a considerable increase in shear rates at the spinneret walls was observed: 12318 s^{-1} and 19709 s^{-1} for low and high extrusions respectively. The results also showed that an increase in the polymer content causes greater shear thinning behavior and causes an increment in the shear

Table 6 Summary of shear rates generated at the outer spinneret walls

DE (ml/min)	Shear rates (s^{-1}) at the spinneret walls			
	25%CA, 37.5% Acetone 37.5% Form.	**25%CA, 45% Acetone 30% Form.**	**27%CA, 36.5% Acetone 36.5% Form.**	**27%CA, 43.8% Acetone 29.2% Form.**
2.5	11239	10582	12318	11233
4.0	17982	16931	19709	17972

rate experienced at the walls of the spinneret. This leads to greater molecular alignment at the surface than in the core, which results in higher oriented membranes being produced. The effect of varying the ratio of acetone to formamide in the dope solution is not as great as that of varying the polymer content. The results seem to explain why the ratio of acetone to formamide is not an important factor and could be pooled as shown in the Taguchi experimental design.(*see* Table 2). The polymer content proved to be an important factor in the production of hollow fiber membranes because of its positive influence in its rheological properties, increasing the shear rates at the spinneret walls, thus promoting molecular orientation at the skin layer and improved separation performance of membrane.

4.0 CONCLUSIONS

The main results presented showed that the morphology is strongly influenced by the rheological properties of the phases and the shear history imposed to the dope solutions. In general, the cellulose acetate dope solution behaves as a shear-thinning power law fluid (index, n in the range of 0.40 to 0.55 and constant, k in the range of 125.32 to 495.85) depending on the cellulose acetate concentration. However the dope polymer solution with the higher polymer concentration exhibit greater shear thinning effect with the index value n of 0.40. This explains for the experimental results using Taguchi Approach where the higher polymer content gives the optimum setting. The shear rate profiles for all the spinning dope solutions in the spinneret annulus at high and low shear rates exhibit skewed curves. The main interest is the level of shear experienced at the spinneret wall. The high extrusion rates results in high shear rates generated at the walls of the spinneret and this leads to greater molecular alignment at the surface than the core which means higher oriented membranes with favourable separation performance.

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