

**SYNTHESIS, CHARACTERIZATION AND  
PERFORMANCE OF POLYSULFONE/  
CELLULOSE ACETATE PHTHALATE/  
POLYVINYLPIRROLIDONE  
(PSF/CAP/PVP) BLEND  
ULTRAFILTRATION  
MEMBRANES**

**ASMADI BIN ALI @ MAHMUD**

**DOCTOR OF PHILOSOPHY  
UNIVERSITI MALAYSIA PAHANG**



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ASMADI BIN ALI @ MAHMUD

Thesis submitted in fulfillment of the requirements  
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I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy in Chemical Engineering.



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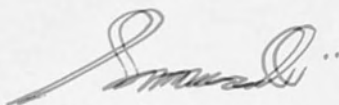
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### DEDICATION

To my mother, late father, wife, and kids..

I would like to thank my mother, late father, wife, and kids for their unconditional love and support throughout my life. I would also like to thank my friends, especially Dr. Mohamed Awwad, Dr. Khalid Hassan, and Dr. Ahmed Elmaghrabi for their encouragement, suggestions, and their effort in making this possible.

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## ABSTRACT

Polysulfone (PSf) is an important class polymer that has been most widely used in the manufacture of synthetic asymmetric ultrafiltration membranes. However, the main disadvantage of PSf membrane is due to its hydrophobic characteristic which in turn fouled the membranes. In practical application of UF systems, membrane fouling is a serious problem that causes high cost energy, operation, and maintenance. Polymer blend is a simple and an efficient method for designing new materials to improve performance of the hydrophobic membranes. The polymer blend is a proven tool to obtain new types of UF membrane, which has better hydrophilicity compared to the original membranes. Cellulose acetate phthalate (CAP) is one of the potential hydrophilic organic polymers that can be used and explored in PSf polymer blend technique to improve hydrophilicity and performance of PSf membranes. PSf/CAP blend membranes with blend composition of 95/5, 90/10, 85/15 and 80/20 wt% of total polymer concentration in the membrane casting solutions were developed via wet phase inversion process. The effect of CAP composition on characteristics, morphology and performance of PSf/CAP blend membranes were investigated. The hydrophilicity of the PSf/CAP blend membranes were improved evidently by blending with CAP. Based on BSA protein separation performance study, the PSf/CAP blend ultrafiltration membrane which contains 10 wt% of CAP shows the best performance membrane due to its high productivity and separation performance as well as it has good membrane characteristics in terms of high hydrophilicity properties, pore properties and membrane morphological structure. The effect of polyvinylpyrrolidone (PVP) additives in the range of 1 to 5 wt% on the best PSf/CAP blend membranes was studied. The results revealed that an addition of 1 to 3 wt% of PVP additive formed membrane with small average pore size and low MWCO due to the strong interpenetrating network between PSf-CAP-PVP and consequently increased protein rejections. Further increment of PVP additive promoted PVP leached out during wet phase inversion process and formed membranes with big pore size and high MWCO. These membranes had high permeate flux but low rejection of proteins. The PSf/CAP/PVP blend membrane that contains 3 wt% of PVP was selected as the best high performance membrane. Further, there were five different shear rates (42.0, 52.5, 70.0, 105.0 and 210.0  $s^{-1}$ ) applied during fabrication process of PSf/CAP/PVP blend membranes by using the best PSf/CAP/PVP dope formulation. The experimental results showed that an increase in shear rate from 42.0 to 105.0  $s^{-1}$  decreased the water content, porosity and permeability of the membranes. Further increment of shear rate to 210.0  $s^{-1}$  increased the water content, porosity and permeability of the membranes due increased in porous structure of PSf/CAP/PVP membrane and a decrease in membrane thickness. In terms of BSA separation performance, the PSf/CAP/PVP blend membranes fabricated at the shear rate of 105.0  $s^{-1}$  showed the best performance due to high rejection of BSA at favorable permeation flux of BSA protein solution. In an evaporation time study, the PSf/CAP/PVP blend membranes fabricated at shear rate of 105.0  $s^{-1}$  were introduced to evaporation time of 5, 10, 15 and 20 s before immersed in a coagulation bath. The results showed that the effects of evaporation time significantly changed the properties and morphological structures of the PSf/CAP/PVP blend membranes. In this experiment study, PSf/CAP/PVP blend membrane which was fabricated at evaporation time of 10 s exhibited the best performance membrane due to high membrane productivity and separation ability.

## ABSTRAK

Polisulfon (PSf) adalah polimer yang penting digunakan dalam pengeluaran membran ultraturasan (UF) asimetrik sintetik. Walaubagaimanapun, kelemahan utama membran PSf adalah ciri hidrofobiknya yang menyebabkan kotoran membran. Secara praktiknya, kotoran membran adalah satu masalah yang sangat serius kerana ia menyebabkan kos tenaga, operasi dan penyelenggaraan yang tinggi. Adunan polimer adalah kaedah paling mudah dan cekap untuk mendapatkan bahan baharu bagi mempertingkatkan prestasi membran hidrofobik. Adunan polimer terbukti sebagai satu cara untuk menghasilkan membran UF baharu yang mempunyai sifat hidrofilik lebih baik berbanding membran asal. Selulosa asetat phthalate (CAP) adalah salah satu polimer organik hidrofilik berpontensi yang boleh digunakan dalam teknik adunan dengan PSf bagi meningkatkan sifat hidrofilik dan prestasi membran PSf. Membran adun PSf/CAP dengan komposisi adunan 95/5, 90/10, 85/15 dan 80/20 wt% dari kepekatan keseluruhan polimer dalam larutan tuang membran dibangunkan melalui proses penyongsangan fasa basah. Kesan komposisi CAP ke atas ciri-ciri, morfologi dan prestasi membran adun PSf/CAP dikaji. Sifat hidrofilik membran adun ini terbukti meningkat dengan mengadunkan CAP. Berdasarkan kajian prestasi pemisahan protein BSA, membran adun PSf/CAP yang mengandungi 10 wt% kandungan CAP dipilih sebagai membran yang terbaik kerana menunjukkan produktiviti dan pemisahan yang tinggi di samping ciri yang baik bagi sifat hidrofilik, sifat liang dan struktur morfologi. Kesan bahan tambah polivinilpirolidon (PVP) dalam julat 1 hingga 5 wt% ke atas membran adun PSf/CAP terbaik dikaji. Keputusan menunjukkan penambahan 1 hingga 3 wt% bahan tambah PVP membentuk membran bersaiz purata liang dan MWCO yang kecil kerana rangkaian saling jalinan yang kuat antara PSf-CAP-PVP dan seterusnya meningkatkan pemisahan protein. Penambahan seterusnya bahan tambah PVP akan menyebabkan PVP melarut resap semasa proses penyongsangan fasa basah dan membentuk membran bersaiz purata liang dan MWCO yang besar. Membran ini mempunyai aliran telapan yang tinggi tetapi pemisahan protein yang rendah. Membran adun PSf/CAP/PVP yang mengandungi 3 wt% PVP dipilih sebagai membran prestasi terbaik. Selanjutnya, lima kadar ricih yang berbeza (42.0, 52.5, 70.0, 105.0 and 210.0  $s^{-1}$ ) digunakan dalam proses pembikinan membran adun PSf/CAP/PVP menggunakan formulasi dop PSf/CAP/PVP yang terbaik. Keputusan ujikaji menunjukkan peningkatan kadar ricih dari 42.0 ke 105.0  $s^{-1}$  menurunkan kandungan air, keporosan dan ketelapan membran. Peningkatan kadar ricih ke 210.0  $s^{-1}$  meningkatkan kandungan air, keporosan dan ketelapan membran kerana peningkatan keporosan struktur membran dan penurunan ketebalan membran. Membran adun PSf/CAP/PVP yang dibikin pada kadar ricih 105.0  $s^{-1}$  menunjukkan prestasi terbaik dengan pemisahan BSA yang tinggi pada aliran yang sesuai. Dalam kajian masa penyejatan, membrane adun PSf/CAP/PVP yang dibikin pada kadar ricih 105.0  $s^{-1}$  didedahkan dengan masa penyejatan selama 5, 10, 15 dan 20 s sebelum direndamkan ke dalam sebuah rendaman penggumpalan. Keputusan menunjukkan kesan masa penyejatan secara signifikan merubah sifat-sifat dan struktur morfologi membran adun PSf/CAP/PVP. Dalam ujikaji ini, membran adun PSf/CAP/PVP yang dibikin pada masa penyejatan selama 10 s menunjukkan membran prestasi terbaik dengan produktiviti dan pemisahan yang tinggi.