ENGINEERING PROPERTIES & STRUCTURE

Newsletter, March 2019

CHAIRPERSON'S REPORT

Dear EPSDIV Members,

I am excited about SPE and EPSDIV as we kick off ANTEC next week. ANTEC is a time of opportunity; it is where experts from industry and academia come together to further knowledge in polymer science and engineering. ANTEC also marks a year of progress for EPSDIV.

During the 2018-19 term, we re-organized EPSDIV into committees to allow us to run more effectively. This has allowed us make progress on all fronts.

Our **Outreach Committee** has a solid year of contribution, from judging posters at the Science and Engineering Fair of Houston, to guiding students at the Texas A&M Materials Science and Engineering Department through career talks.

Our **Knowledge Sharing Committee** is tasked with our primary goal of furthering science and engineering. Our TPCs Mohammad Hossain and Ying Shi have led the creation of an excellent Antec program, which I hope all of you will enjoy in Detroit. The Knowledge Sharing Committee has also been working on new forms of programming for our members, which we will roll out in the coming year.

Our **Communications Committee** has kept up with regular Newsletters, while stretching us to employ social media more frequently. We appreciate Paul Hans' dedication on this front, and encourage our members to contribute with articles.

Our **Awards Committee** has had a successful year. We have contributed to the SPE International Award, are hosting the EPSDIV Best Paper Award, sponsoring student activities at ANTEC2019, and have made several nominations for Fellow of the Society. This year, we are honored to celebrate Stephen H. Carr's recognition as SPE Fellow.

Our **Finance Committee** is facilitating the transition of the treasurer role from Emmett Crawford to Sean Teller. Emmett served EPSDIV as treasurer for a number of years, and we appreciate all his contributions. Emmett will stay on the EPSDIV board, perhaps taking on new leadership roles, as Sean takes on the treasurer role starting at ANTEC.

With every passing ANTEC, EPSDIV continues to evolve. We are pleased to welcome our newest board members Kat Wakabayashi, Jia Wang and Ed Fewkes. As I pass the flag of EPSDIV Chair to Pavan Valavala, I am confident that the EPSDIV committees will become even more productive in the 2019-2020 term.

Do not forget to join us at this year's **EPSDIV Reception**, March 19, 6:00-7.30 PM, 5th floor inner circle, Marriott Renaissance Center.

Have a wonderful ANTEC 2019!

Kaan Gunes, Ph.D.
2018-19 EPSDIV Chair

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ENGINEERING PROPERTIES & STRUCTURE

See you at ANTEC 2019!

The 2019 annual technical conference (ANTEC) of the Society of Plastics Engineers (SPE) will be held March 18-21 in Detroit, Michigan. The ANTEC organizing committee has worked diligently to update the format to meet evolving membership needs. The new format strikes a balance between technical sessions covering research and development in the plastics arena, and market facing sessions focused on the latest trends in packaging, building and construction, and transportation, with a sustainability slant. Sustainability is manifested in many different formats in the plastics world be it in the form of tougher polymers to enable fabrication of thinner, flexible packaging to reduce material consumption, while also reducing food wastage by preserving and protecting the food from farm to table. Or tougher resins to fabricate plastic pressure pipes to replace cracked, corroded existing infrastructure, thereby reducing water wastage. Other aspects of sustainability such as environmental consciousness has also led to package simplification and recyclability.

The Engineering Properties and Structure Division (EPSDIV) will host five technical sessions at ANTEC 2019, including a tutorial/training session on fundamentals of structure-property relationship with a focus on rheology.

EPSDIV board members also supported community STEM (science, technology, engineering and mathematics) activities by participating as judges in the 60th Science & Engineering Fair of Houston (SEFH) on Saturday, February 23, 2019. SEFH serves as the regional fair for junior and senior high school students providing them an opportunity to apply their mathematics and science knowledge beyond the classroom. The overall team of judges conducted nearly 3000 interviews to evaluate more than 700 student projects across two divisions and 17 project categories. Based on the feedback received from students, parents, teachers, and the judges, SEFH 2019 was an overwhelmingly positive experience for all participants.

We are actively looking for new members to join EPSDIV. If you are passionate about the work you do, interested in giving back by volunteering or educating the community, want to expand your network or simply stay abreast of the latest developments in the plastics industry, come join EPSDIV.

You can take advantage of ANTEC to meet the board members in person at the Technical Program Committee (TPC) Meeting, March 19, 12.30 to 1.30 PM, Richard, or at the EPSDIV Reception, March 19, 6:00-7.30 PM, 5th floor inner circle, Marriott Renaissance Center.
See you at ANTEC 2019!

Babli Kapur

ENGINEERING PROPERTIES & STRUCTURE

EPSDIV ELECTION RESULTS

Three new Board Members!

Congratulations to Katsuyuki (Kat) Wakabayashi (Bucknell University), Jia Wang (SC Johnson and Son, Inc.) and Ed Fewkes (Corning, Inc.) for their election to the Board of Directors! Their three year term starts at ANTEC2019.

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Many thanks to our Donors!

Your generous support is greatly appreciated!

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OUTREACH COMMITTEE

ENGINEERING PROPERTIES & STRUCTURE

The Outreach Committee of EPSDIV (the Engineering Properties and Structure Division) is focused on giving back to the community.

Recently, Pavan Valavala (EPSDIV Chair-elect 2019-2020), Babli Kapur (EPSDIV Councilor), and Kaan Gunes (EPSDIV Chair 2018-2019) volunteered as judges at The Science Engineering Fair of Houston (SEFH 2019).

SEFH is a not-for-profit educational organization that provides a unique and beneficial science educational service to Junior and Senior high school students in grades 7-12.

SEFH serves as the regional fair for all junior and senior high school students in Harris County Texas and 22 surrounding counties. Major regional fair winners are eligible to compete in the annual International Science and Engineering Fair (ISEF).

Thanks Pavan, Babli and Kaan!

Possible ideas for Community Outreach:

- Teaching a science class on polymers, math or engineering.
- School Science Fairs
- Volunteering in a food pantry.
- Cleaning a section of a highway as a group.
- Helping out at an animal shelter.
- Habitat for Humanity.
- Libraries, Red Cross, Retirement Homes.

Please share your ideas about possible outreach opportunities by sending an email to the newsletter editor. We will put them in the next newsletter.
paul.hans@polyone.com

If you participate in an outreach effort, please email some details about the activity and a few pictures!

COMMUNICATIONS COMMITTEE

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Hi everyone! You'll notice a few new sections in the newsletter based on feedback from readers. The ***Interesting Links*** page has reader submitted links to stories that they found interesting. Please send me any links you find interesting.

A new section this month is ***Professor's Corner***. Thanks to Professor Katsuyuki (Kat) Wakabayashi for providing the inaugural page. We have many academics in the EPSDIV and we thought it would be good to give them a one-page format to tell us what their interests are, a little about their school, etc. Thinks of this as a networking opportunity. If you are interested in being in the July/August (or future) newsletter send me an email!

The ***Outreach Committee*** also has their inaugural page in this newsletter. Three EPSDIV members volunteered as judges for the 60th Science & Engineering Fair of Houston (SEFH). Send me an email (and a few pics!) of you and your friends giving back to the community!

As always, please let me know your ideas for improving the newsletter. Thanks!

Paul Hans (paul.hans@polyone.com)

Katsuyuki (Kat) Wakabayashi
Associate Professor of Chemical Engineering
Bucknell University (Lewisburg, Pennsylvania)

Website | LinkedIn

The College of Engineering at Bucknell University is #6 in the most recent U.S. News and World Report ranking among the 205 engineering colleges not offering Ph.D. degrees. In relevant majors,

- Chemical Engineering is ranked #1
- Biomedical Engineering is ranked #1
- Mechanical Engineering is ranked #3

Bucknell campus is quaint and beautiful—please visit!

Prof. Wakabayashi's research projects focus around the unique processing technique called solid-state shear pulverization (SSSP), with which they process…

Homopolymers (molecular modification)
Polymer blends (compatibilization, homogenization)
Polymer composites (dispersion, distribution)
Polymer nanocomposites (exfoliation, distribution)
Others (size reduction, dissolution, reaction)

…for a wide range of target applications.

Bucknell is a predominantly undergrad institution, so the Wakabayashi research lab often has only undergraduate students. While they have support from the University for research, they also seek real-world experience through summer internships—please help them out!

Prof. Wakabayashi's lab works on fundamental research to publish journal articles (this and others in SPE journals especially in Polym. Eng. Sci. and Polym. Compos.), as well as industrial collaboration-based applied research (and sometimes work on patents like this). Please be on the look out for a new Plastics Design Library Series book "Solid-State Shear Pulverization" (Elsevier), to be published in the near future!

Come Join SPE & EPSDIV ! !

We are actively looking for new members to join EPSDIV.

Are you:

- Passionate about the work you do?
- Wanting to stay abreast of the latest developments in the plastics industry?
- Interested in giving back by volunteering or educating the community?
- Wanting to expand your network?

Pass this newsletter onto a friend and encourage them to choose EPSDIV as their Division

JOIN SPE

Do you like to write?

The Communications Committee is looking for individuals interested in writing technical articles for the newsletter. If you have an interest in this please send me an email describing your thoughts for an article in general terms.

Interested parties could be individual contributors who have interest in a topical area, a consultant, or a supplier interested in explaining a particular material, instrument, technique, etc.

Thanks!

Interested in writing

ENGINEERING PROPERTIES & STRUCTURE

From the Technical Program Committee Chairs:

The Engineered Properties and Structure Division will have 4 sessions on Monday and Tuesday (morning and afternoon) and a tutorial session on Applied Rheology on Wednesday.

Session	Topic
Monday Morning	Structure-property relationships in composites
Monday Afternoon	Structure-property relationships in polymers and blends
Tuesday Morning	Scratch and wear behavior of polymers
Tuesday Afternoon	Polymer characterization & modeling
Wed Morning	Training/Tutorial session on rheology

We are looking forward to seeing everyone at ANTEC in Detroit!

EPSDIV TPC Co-Chairs
Dr. Ying Shi (Ying.Shi@aschulman.com)
Dr. Mohammad Hossain (Mohammad.Hossain@tamuk.edu)

IMPORTANT ANTEC MEETINGS—DAYS/TIMES

EPSDIV Board Meeting: Sunday, March 17th, 2019, 5pm—6:30pm (rm: Richard A & B)

TPC Meeting and Luncheon: Tuesday, March 19, 2019, 12:15pm—1:30pm (rm: Richard)

EPSDIV Reception: Tuesday, March 19, 2019, 6pm– 9pm (rm: 5th Floor Inner Circle)

TREASURER'S REPORT

FINANCIAL REPORT FROM
JULY 1, 2018 TO FEB. 22, 2019

BALANCE as of July 1, 2018 **$ 30,739.58**
(cash, checking, savings, investments)

INCOME	**ACTUAL**
SPE Rebate	$ 3480.00
Misc. Income	$ 768.50
Education, Technical & Newsletter Donors	$ 2443.50
TOTAL INCOME	$ 6692.00

EXPENSES	
Awards	$ 2500.00
Councilor Travel	$ 687.56
Student Travel Fund	$ 500.00
TOTAL EXPENSES	$ 3687.56

CASH FLOW	$ 3004.44

ENDING BALANCE
as of April 10, 2018 **$ 33,744.02**

Submitted by Emmett Crawford, EPSDIV
Treasurer 2018-2019

EPSDIV EDUCATION, TECHNICAL AND NEWSLETTER DONOR PROGRAM

For the modest sum of $500 your company will get:

- **Two FREE** 1/2 page ad spaces in Newsletter—a $500 value!!
- Reduced rates on additional advertising.
- Your Company name or logo on presentation screen between EPSDIV sponsored talks at ANTEC meeting!
- Your Company name listed In newsletter for a running 2-year period (3-4 issues per year).

Click here to become a donor today!

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Funds from the program are used to support the EPSDIV mission in several key areas:

- **Plastics education**

  Such as, sponsorship of awards for outstanding student papers, student travel grants, scholarships and short courses.

- **Technical program quality**

  Such as, sponsorship of awards for outstanding papers, expenses and honoraria for invited speakers, and seed money for RETECs and other EPSDIV sponsored symposia.

- **Newsletter distribution & quality**

Please ask your company or organization to become a donor to the 2019 program! Thank you!!

INTERESTING LINKS

ENGINEERING PROPERTIES & STRUCTURE

Is there an interesting link you would like to share? Send it to the newsletter editor by clicking **>>here<<**.

We will put it in the next newsletter. Thanks!

The energy implications of organic radical polymers. The main appeal is the speed of the reaction. These polymers are able to charge and discharge very fast. (Source: Texas A&M)

https://engineering.tamu.edu/news/2018/11/the-energy-implications-of-organic-radical-polymers.html

A team of engineers in the McKelvey School of Engineering at Washington University in St. Louis has developed a high-power fuel cell that advances technology in this area.

https://source.wustl.edu/2019/02/high-powered-fuel-cell-may-boost-electric-powered-drones-aircraft/

Biodegradable water bottle will melt away if it ends up in the ocean.

https://www.fastcompany.com/90304442/this-new-water-companys-compostable-bottle-fully-biodegrades-in-the-ocean

3d-Printed rubber self heals itself.

3D printed rubber

Engineers develop ingestible pill that monitors stomach for 30 days.

Ingestible pillswells in stomach

Graphene Implants Record Low-Level Electrical Brain Activity

Graphene implants brain activity

New Coating Repels Ice from Any Surface

Breakthrough in Ice-Repelling Materials

ENGINEERING PROPERTIES & STRUCTURE

Congratulations to ANTEC 2018 EPSDIV Best Paper WINNERS:

Gerald Billovits
The Dow Chemical Company, Midland MI

AND

Ji Eun (Jamie) Lee
York University, Toronto ON

Jamie Lee's paper was re-printed in the December 2018 newsletter. In this issue of our newsletter we are re-printing Gerry Billovits' paper. Thanks to both for sharing their work!

December 2018:

CRYSTALLIZATION MECHANISM OF POLYVINYLIDENE FLUORIDE VIA NON-ISOTHERMAL CRYSTALLIZATION AND SUPERCRITICAL CO_2 PROCESSING

Ji Eun Lee and Siu N. Leung, Lassonde School of Engineering,

Department of Mechanical Engineering, York University, Toronto, ON, Canada

March 2019:

Microcapillary Film Membranes based on Polyvinylidene Fluoride

Gerald Billovits, David Moll, Joseph Dooley, Calvin Pavlicek, Tom Parsons, Clifford Todd, and Thomas Fisk, The Dow Chemical Company, Midland, MI

Microcapillary Film Membranes based on Polyvinylidene Fluoride

Gerald Billovits, David Moll, Joseph Dooley, Calvin Pavlicek, Tom Parsons, Clifford Todd, and Thomas Fisk, The Dow Chemical Company, Midland, MI

Abstract

Microcapillary film (MCF) membranes offer a promising new media configuration for water purification devices. A 50 mm wide microcapillary film die was designed and constructed, allowing a fluid to be injected at 42 separate locations within a molten polymeric film as it exited the die. MCF membranes were prepared using this die by profile extrusion of a polyvinylidene fluoride (PVDF) based formulation, which was rendered microporous via Thermally Induced Phase Separation (TIPS) and dissolution of a dispersed *nano*-calcium carbonate porogen. Air was used as the bore fluid to form the microcapillaries. Analysis of the membranes prepared by this technique using scanning electron microscopy showed surface porosity and an interconnected, porous interior morphology that was uniform from the outside surface to the capillaries on the interior. These MCF membranes can be formed into spiral wound modules, useful for ultrafiltration applications or, when coated with an ion-rejecting top layer, for desalination of aqueous feed streams.

Introduction

Microcapillary film (MCF) membranes present an interesting variation on conventional microporous structures. The preparation of microcapillary films and their applications was pioneered by Professor Malcolm Mackley and his students at Cambridge University [1-6]. Bonyadi and Mackley [7] extended these structures to porous systems, creating ethylene-co-vinyl alcohol (EVOH) MCF membranes via the diffusion induced phase separation (DIPS) process. They extruded polymer solutions containing EVOH along with polyvinylpyrrolidone (PVP) dissolved in N-methylpyrrolidine (NMP), using glycerol as the bore fluid to form the capillaries, and quenching into an aqueous bath. Similarly, Peng et al., [8] extruded MCF ultrafiltration membranes from solutions of polyacrylonitrile (PAN) in NMP, which were also quenched via the DIPS process into water or water alcohol mixtures, using water/NMP mixtures as the bore fluid. Finally, Teoh et al., [9] prepared microporous MCF membranes derived from polyvinylidene fluoride (PVDF) using the DIPS process for applications in membrane distillation of seawater. They extruded formulations containing PVDF and an organoclay in a mixture of NMP with ethylene glycol into an aqueous quench bath, using NMP/ water (1/1) as the bore fluid. In all of these cases, significant deformation of the MCF structure and undulations in the surface accompanied the DIPS membrane formation process.

PVDF Membranes via TIPS

Polyvinylidene fluoride has found significant utilization as a membrane-forming material due to the combination of excellent chemical resistance, high mechanical strength, and reasonable hydrophobicity. In their excellent review, Liu et al., [10] described a variety of different membrane structures formed from this polymer using standard membrane formation techniques. PVDF is soluble at room temperature in a number of common organic solvents, including N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), and acetone, and these PVDF solutions can be de-stabilized by immersion in various non-solvents via the DIPS process, to form porous structures. Alternately, several high boiling point solvents or their mixtures, most notably various phthalate esters, can act as solvents at higher temperatures, but non-solvents at lower temperatures, thereby exhibiting upper critical solution temperature (UCST) behavior. Thermally induced destabilization caused by reducing the temperature of a homogeneous polymer solution via the TIPS process is a convenient method for creating porous structures since it only relies on heat transfer with a polymer solution, rather than molecular diffusion of a non-solvent agent. For semi-crystalline polymers like PVDF, this destabilization can result in solid/liquid (S-L) phase separation, where the polymer crystallizes directly from solution, or liquid/liquid (L-L) separation, where the continuous, polymer-rich matrix phase is initially fluid, but rapidly solidifies with further cooling due to crystallization of the polymer component.

Several researchers have prepared microporous PVDF membranes via TIPS. Lloyd et al., [11] employed dibutyl phthalate (DBP) as a diluent for the preparation of microporous PVDF membranes, but observed fuzzy, spherical structures formed by S-L TIPS in their study. Similarly, Gu et al., [12] investigated the effect of several high boiling ester solvents and quenching conditions on the membrane morphology. They also found spherulitic-dominated morphologies and attributed the observed variations to the effect of polymer-solvent interaction strength on crystallization of the PVDF. A number of researchers have also utilized blended solvent systems,

especially mixtures of different phthalate esters, to optimize the temperature dependent phase behavior of PVDF solvent systems.

In this study, microcapillary film membranes were prepared from a formulation that created a porous structure via a thermally induced phase separation (TIPS) process, augmented by a dissolvable nano-porogen. Figure 1 shows the basic sequence of process steps utilized to create microporosity in the MCF structure.

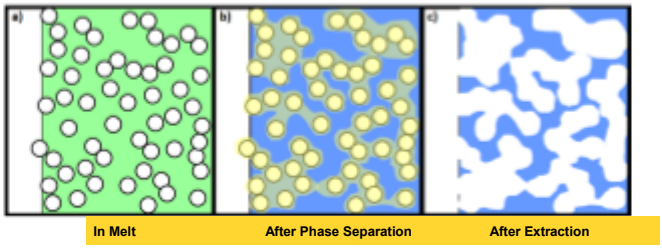

Figure 1. Schematic representation of the concept underlying the use of a nanoparticle porogen in a TIPS membrane formation process.

In Figure 1, the left cartoon shows the situation at high temperature where the polymer and diluent form a single liquid phase. In this image, the nanoparticles, shown as white circles, are well dispersed within the homogeneous (green-colored) polymer solution, thereby increasing the viscosity of the formulation. The center cartoon illustrates conditions after the film enters the quench bath and the temperature of the formulation has decreased below the cloud point. The homogeneous solution has separated into a polymer-rich (blue) and a diluent-rich (yellow) phase. If the surface energies are favorable, the polymer-depleted phase surrounds the nanoparticles. Further cooling locks in this structure via crystallization of the polymer component in the matrix phase. In the cartoon on the right, both the nanofiller and the diluent-rich phase have been removed via an appropriate dissolution/extraction process, yielding an open, continuous structure with a high void fraction.

Materials

Extrusion runs to prepare microporous microcapillary films were performed using a polymer/diluent formulation that forms uniform porosity via the TIPS process. It was based on a medium viscosity polyvinylidene fluoride homopolymer resin powder. The diluent system consisted of a mixture of phthalates to control the phase separation temperature and porosity. As shown in Figure 1, the pore volume in this formulation was expanded through the use of a precipitated calcium carbonate powder.

Shortly before extrusion, the components were charged to a Henschel mixer (Purnell International, Houston, TX) and mixed briefly (~30 sec) to disperse the components into a flowable, powdered masterbatch.

Microcapillary Film Die

A laboratory-scale microcapillary film die was designed and fabricated based on guidelines described by Mackley et al., [1] as well as general die design best practices. It consisted of a two-part "clam shell" housing design with streamlined flow paths and gentle angles. A separate, replaceable insert was also designed to inject air into the polymer stream at a number of discrete locations just as the molten film exited the die. Figure 2 a) shows a photograph of the air injection insert, which fits into a corresponding cavity near the outlet of the die as shown in the rendering in Figure 2 b). This insert had a diamond shaped cross section, which split the polymer flow into two separate streams that flow above and below the insert and recombined just before exiting the die. The interior of the insert had a "teardrop-shaped" cavity extending the full width of the die. The individual needles were fabricated from 25 Gauge stainless steel dispensing needles (McMaster-Carr, P/N 6710A33), which have an outside diameter of 0.508 mm and an inside diameter of 0.254 mm. These were welded into a row of 42 equally spaced, predrilled holes at the forward edge of the insert, which connected to the interior cavity to create a manifold. When the air insert is installed in the clamshell die, the outlet of the needles ends within 25 µm of the die exit in the polymer flow path.

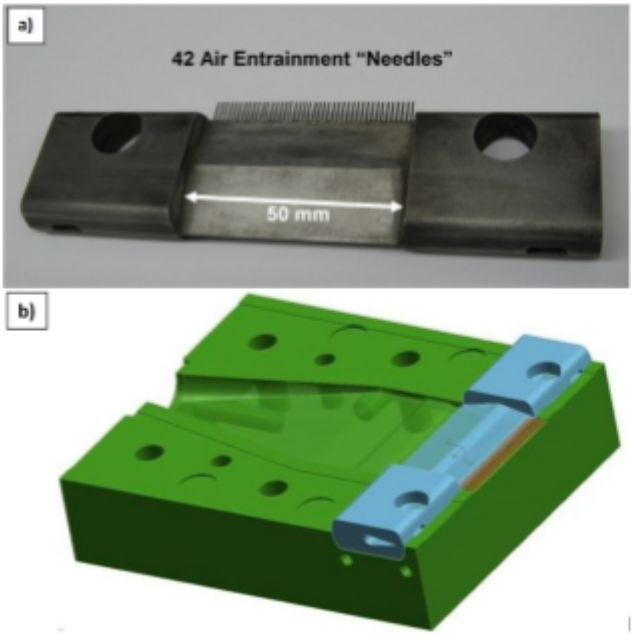

Figure 2. a) Photograph of the air injection insert showing the 50 mm wide polymer melt flow path and the 42 air entrainment "needles"; **b)** Rendering of open MCF die showing the position of the insert near the die exit.

After installing the air insert, the twin halves of the clam shell die were bolted together. The whole MCF die assembly was heated with bolt-on aluminum plates containing pencil-style heating elements. In operation, the 50 mm MCF die was oriented with the film exit pointed downward. It was connected to the extrusion apparatus described below through a custom elbow adapter, which was designed with circular flow path cross sections and a gentle radius with no dead spots in order to minimize degradation and separation of the formulation components.

Microcapillary Film Extrusion

The Microcapillary Film die described above was attached to a twin screw extruder-based compounding apparatus. As shown in the schematic representation in Figure 3, the apparatus consisted of a 25 mm twin screw extruder (Coperion ZSK-25 MEGA) with L/D = 37.8, followed by a gear pump (10.3 cm^3/rev, Pressure Systems Inc.) with manual speed control.

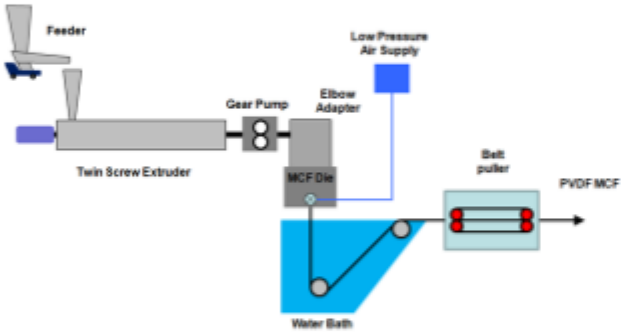

Figure 3. Schematic representation of the microcapillary film membrane extrusion process.

The extruder setup consisted of 9 barrel segments and utilized a screw design incorporating multiple sets of kneading blocks and other mixing elements to efficiently disperse the components without overheating the melt. All ports in the barrel segments were sealed with plugs except for the feed port in Barrel #1 and an atmospheric vent in Barrel #8 for degassing air and other volatiles. The powdered PVDF masterbatch feed was charged to the extruder using a vibrating tray, loss-in-weight feeder. The molten polymer film, which exited downward from the MCF die, was pulled over a pair of rollers and quenched in a water bath. The quenched film exiting the water bath was pulled at a controlled linear velocity using a belt puller equipped with a variable speed control.

Microporous Microcapillary Films

The PVDF-based, TIPS membrane generating formulation was fed to the MCF extrusion apparatus at a feed rate of 3.41 kg/hr. Using slight positive air pressure to the air injection insert, microcapillary films were successfully extruded at a melt temperature of 200 °C. Due to the high melt strength of the filled formulation, very little melt draw was observed in the 3 inch air gap between the die and the water bath at low linear speeds (0.6-1.0 m/min). The extrusion process showed good stability, enabling the collection of long lengths of PVDF-based, phase separated, MCF films. Figure 4 shows a photograph of the cross section of one of these films, displaying 40 open microcapillaries with good uniformity; one partially open capillary and one plugged capillary are also seen in this image.

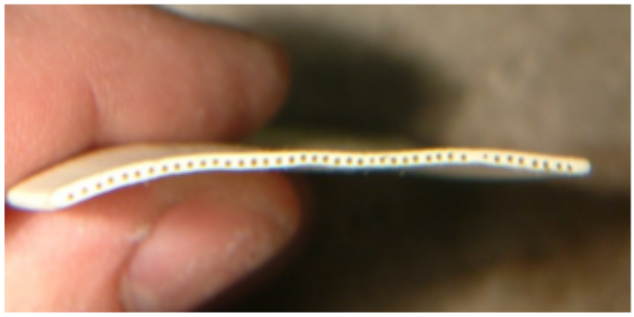

Figure 4. Photograph of the cross section of an extruded, PVDF-based MCF film.

Sections of extruded, quenched films were then extracted in borosilicate glass trays to develop the porosity using a two stage process. In the first step, the phthalates, which have low solubility in water, were extracted by submerging the films in methanol or ethanol at ambient temperature; the trays were covered with plastic film to retard evaporation of the solvent and stored in a lab hood overnight. In the second step, the calcium carbonate nanoparticles were dissolved by immersing the alcohol-extracted films in 5-10 % aqueous HCl solution. The acidic liquid diffused into the pores in the film and digested the water-insoluble $CaCO_3$ particles, generating carbon dioxide, and solvating the Ca^{2+} ions in the aqueous phase. During the digestion process, vigorous gas evolution was observed from both surfaces of the film and also from the open ends of the microcapillaries. After bubbling had ceased, the extracted films were leached in deionized (DI) water, which was replaced several times, until the pH of the water had increased to at least 4.5.

Porosity in the fully extracted MCF films was characterized by scanning electron microscopy (SEM). Figure 5 shows a low magnification SEM image of a fully extracted MCF film showing the top surface and cross section after freeze fracturing in liquid nitrogen. Several open, cylindrical capillaries with a diameter of 500 µm are seen in the ~1 mm thick cross section.

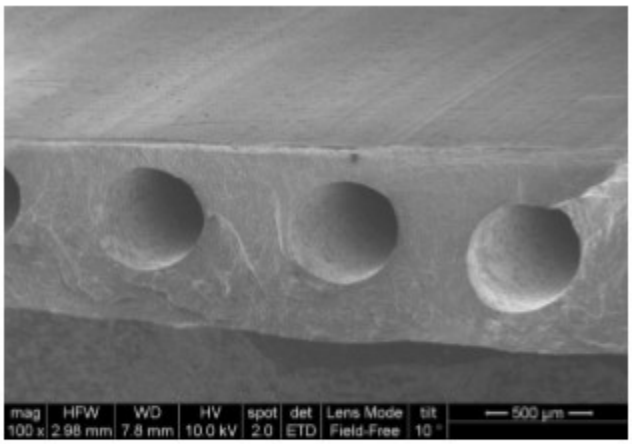

Figure 5. Low magnification SEM photomicrograph of a freeze-fractured, microporous, PVDF-based MCF film.

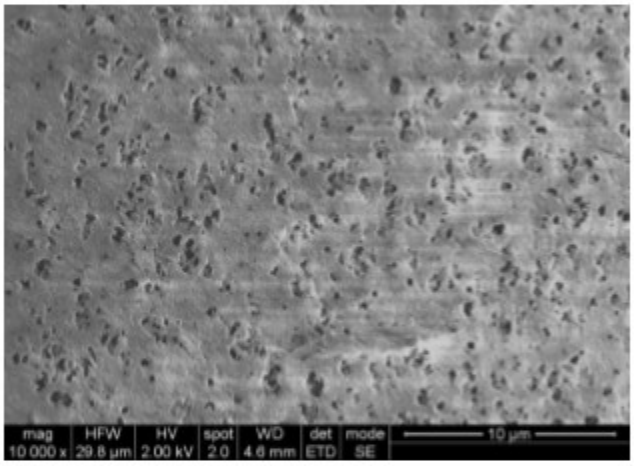

Figure 6. SEM photomicrograph of the surface of a microporous, PVDF-based MCF film.

Figure 6 shows a SEM photomicrograph of the top surface of a microporous MCF film. This image displays a high areal density of overlapping pores with diameters up to ~500 nm. The porous nature of the interior of the film can be seen in Figure 7, which shows a higher magnification SEM photomicrograph of the cross section near a microcapillary. This image also clearly shows the open pores on the interior surface of the microcapillary. A higher magnification SEM image showing the interconnected, submicron pores in the interior of the film is shown in Figure 8.

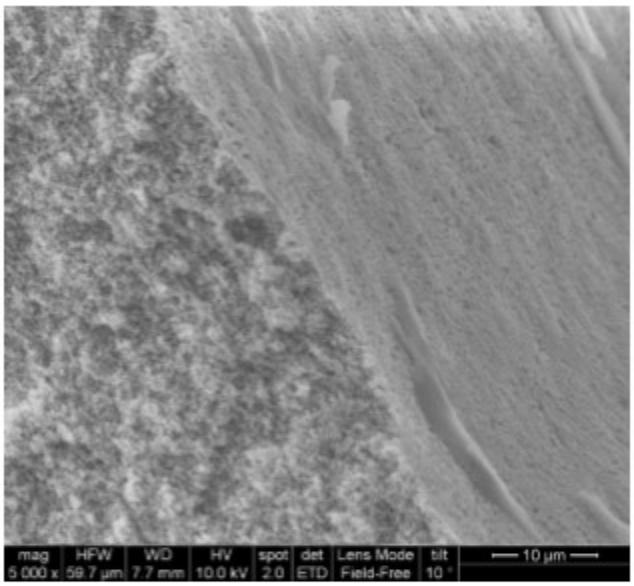

Figure 7. SEM photomicrograph of a freeze-fractured cross section of a microporous, PVDF-based MCF film, showing the interior of a microcapillary.

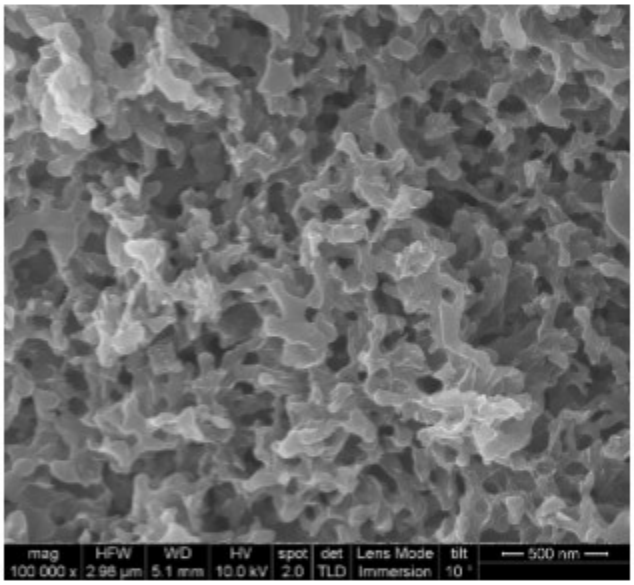

Figure 8. SEM photomicrograph of a freeze-fractured cross section of a microporous, PVDF-based MCF film, showing the interconnected submicron pores.

Flux Measurements on MCF Films

Conventional, flat membrane test cells typically measure the flux of water through a thin, porous sheet. While the permeability of microcapillary film membranes could be characterized using such an apparatus, the fluxes measured would not probe the desired flow path. The unique geometry of the microcapillary film membranes

required the design and fabrication of a custom apparatus for measuring the transport of water in through the two flat membrane surfaces and out through the microcapillaries.

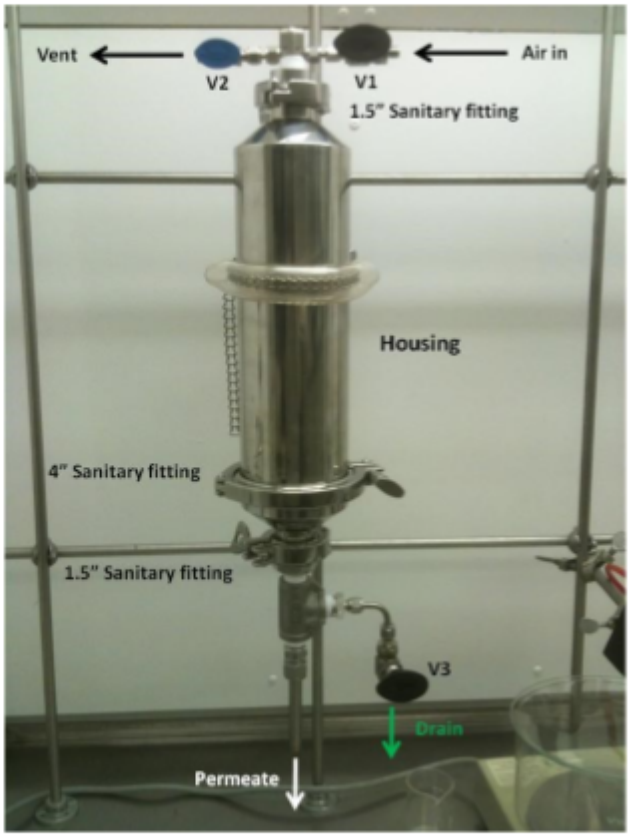

Figure 9. Photograph of the MCF membrane flux tester.

Figure 9 shows the Microcapillary Film membrane flux tester, which was assembled to characterize the pure water permeability (PWP) of MCF membranes. The apparatus was based on a pressure vessel housing that functioned as a reservoir for the feed water and held the MCF membrane to be tested. Figure 10 shows the interior of the housing with a mounted microcapillary film membrane. The MCF test sample was attached to a custom slotted holder, which was connected to a permeate collector tube that extended to the exterior of the device.

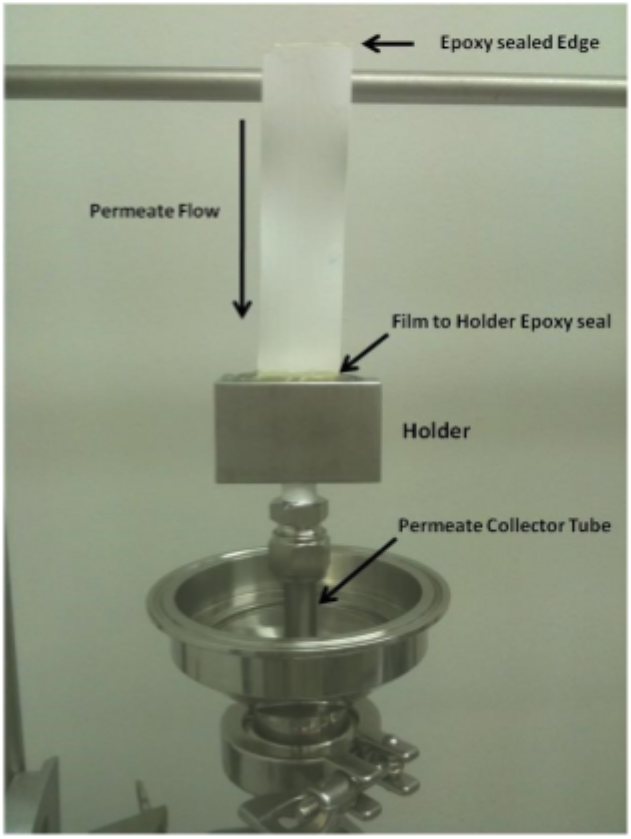

Figure 10. Photograph of the interior of the MCF membrane flux tester.

Extracted MCF films up to 13 cm long were inserted into the slot in the holder and sealed with a bead of epoxy. The opposite, open end of the MCF film was also sealed with epoxy.

In order to characterize the pure water permeability, the pores in the mounted MCF membrane were first wetted well by completely immersing the test fixture in an aqueous solution containing 25 % isopropanol for 30 minutes. The test fixture was then rinsed with DI water and installed in the housing. After filling the reservoir with DI water through the top port, actual flux measurements were made by setting the inlet air pressure to a desired value and measuring the permeate flux gravimetrically for a period of 10 minutes or until 800 g of permeate was collected. This flux testing was performed at 3 pressures, typically 0.68, 1.36, and 2.04 bar (10, 20, and 30 psig), within the desired range. The housing was refilled with DI water after each test to insure that the entire membrane surface remained fully submerged throughout the test.

Figure 11 shows a plot of Permeate Weight (g) vs. Time (min), showing data for flux tests performed at three different applied pressures for a particular PVDF-based

MCF sample with a total (two sided) membrane area of 106.68 cm^2.

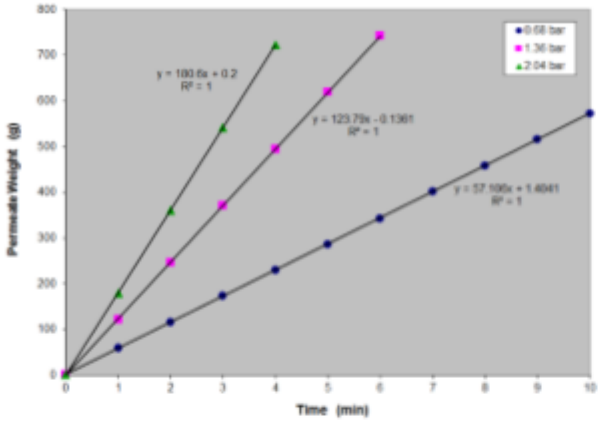

Figure 11. Plot of permeate mass discharged from the capillaries vs. time for a PVDF-based MCF film with a total area of 106.68 cm^2, mounted in the MCF flux tester

For all three pressures, the data show a high degree of linearity; the slope of the fitted lines gives the permeate mass flux, $\dot{m}$, measured as g/min for each pressure. The mass flux can be used to calculate the Pure Water Permeability (PWP), expressed as L/m^2 h bar, using the following expression:

$$PWP = 600\frac{\dot{m}}{\rho A p} \qquad (1)$$

Here ρ is the density of water (i.e., 1.00 g/cm^3), A is the total membrane area (in cm^2), p is the applied pressure (in bar), and 600 is a lumped constant that accounts for the conversion factors. Table 1 applies Eq. 1 to the data shown in Figure 11.

Table 1. Pure Water Permeability for a PVDF-based MCF membrane with a total surface area of 106.68 cm^2 as measured with the MCF flux tester.

Pressure (bar)	Permeate Flux (g/min)	PWP (L/m^2·h·bar)
0.68	57.106	472
1.36	123.79	512
2.04	180.60	498

The data in Table 1 for this particular MCF membrane do not show a consistent trend with applied pressure; the mean value for the pure water permeability was 494 L/m^2 h bar. Variation in the calculated PWP values is likely due to uncertainty in the pressure measurement, which was estimated to be ±2 psi (0.14 bar) with the 0-100 psig pressure gauge used.

Conclusions

Microcapillary film (MCF) membranes were prepared by profile extrusion of a polyvinylidene fluoride (PVDF) based formulation using a newly designed 50 mm wide MCF die. Air was injected at 42 separate points within the molten film to create the microcapillaries. The extruded films were rendered microporous via Thermally Induced Phase Separation (TIPS) and dissolution of a dispersed *nano*-calcium carbonate porogen.

Analysis by scanning electron microscopy showed porous surfaces and an open, porous interior morphology that appeared uniform from the outside surface to the capillaries on the interior.

The pure water flux was determined for these membranes using a specially designed test apparatus that measured the water flux going in through both lateral surfaces and out through the microcapillaries. The mean pure water permeability measured by this technique was 494 L/m^2 h bar. The MCF membranes so produced are anticipated to be useful in spiral wound modules for the removal of particulates from fluids and as supports for thin film composite reverse osmosis membranes.

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