TPM&F

THERMOPLASTIC MATERIALS AND FOAMS DIVISION

HTTP://SPETPMF.COM/

TPM&F SCOPE

The Thermoplastic Materials and Foams Division is organized to provide a focal point for the interchange of information relating to non-vinyl thermoplastic resins including fluoropolymers, polyamides, polyesters, polyolefins, polystyrenes, polyurethanes, their filled and/or reinforced products, and their foamable and foamed products. Its interests lie in stimulating the development of scientific and engineering knowledge. By encouraging participation between producers and consumers, it aims to provide information on new developments which shall encompass synthesis, characterization, fabrication, safe handling, application, serviceability, and marketing.

Communications Excellence Award

Pinnacle Award

The Society of Plastics Engineers
6 Berkshire Blvd, Suite 306
Bethel, CT 06801
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CHAIRMAN'S MESSAGE

DECEMBER 2018

Dear fellow SPE TPM&F Division members,

I bet everyone had a great Thanksgiving break! On behalf of the SPE TPM&F board of directors, I wish everyone enjoy the rest of the holiday season. Everyone deserves some relaxing time from the hard work and get together with families & friends.

Looking back at the year 2018, in February we kicked off the year-long wonderful SPE TPM&F programs with the Polyolefins 2018 conference in Houston. In May we had the great ANTEC® conference in Orlando. Coming into September, our annual FOAMS® conference was successfully held in Montreal, Canada. I really appreciate the great work by the leaders for those flagship TPM&F programs: Donna Davis for Polyolefins Conference, Prof. Chad Zeng for ANTEC® conference, and Dr. Stephane Costeux for FOAMS® conference. We recognized our 2017 Outstanding Achievement Award (OAA) recipient Dr. S.T. Lee in ANTEC® 2018 and the 2018 OAA recipient Dr. Jim Throne in FOAMS® 2018. We are proud of the significant achievements of our own board directors: Professor Masahiro Ohshima being appointed the Dean of the Engineering School and the Graduate School of Engineering at Kyoto University; Donna Davis being inducted to Plastic Hall of Fame in the NPE/ANTEC® 2018.

Led by our Education Committee Chair Dr. Kim McLoughlin, TPM&F spent a great deal of resources on students. Multiple TPM&F scholarships were offered, including Chatterjee Travel Awards, Salvatore J. Monte Scholarship, and Michael Reedy TPM&F Scholarship. In honor of our long-term Board Director Ray Shute who passed away earlier this year, we will establish a Raymond Shute Scholarship in 2019. In addition, we sponsored the Plastics and Poly-

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CHAIRMAN'S MESSAGE - CONTINUED

mer Engineering Technology Department at Pennsylvania College of Technology for a student tour (8 students and 2 faculty members) of five plastics material suppliers in the Pittsburgh area. Another TPM&F sponsored event is the PlastiVan in Pittsburgh in October 2017. TPM&F grant also enabled a Student Paper Contest in U of Toronto.

In this newsletter please enjoy the full-text papers for our two best papers: TPM&F ANTEC® 2018 Best Paper "Protected biofilm growth in macroporous polyvinylidene fluoride carriers for biological organic removal from municipal wastewater"; and the FOAMS® 2018 Best Paper "IMPROVEMENT IN MORPHOLOGY AND MECHANICAL PROPERTIES OF EXTRUDED POLYSTYRENE FOAMS WITH TRISAMIDE BASED ADDITIVES". Congratulations again to the authors!

Dr. Xiaoxi Wang
SPE TPM&F Division Chair

NEWSLETTER PUBLICATION SPONSORSHIP INFORMATION

Sponsorship size allocations
(1 year, 3 issues):

BC size: **$375**
3.500" wide x 2" high

1/4 page size: **$675**
3.875" wide x 5" high

1/2 page size: **$1,125**
7.750" wide x 5" high

If you are interested in sponsoring our newsletter, please contact:
Aaron Guan
aaron.guan@bocotechnology.com

ANTEC® 2019 PROGRAM IN THERMOPLASTIC MATERIALS & FOAMS DIVISION

MARCH 18 Tuesday AM

DULUTH ROOM, 9:00 AM - NOON

TITLE

Piezoresistive Polymer Nanocomposites and their Foams as Smart Sensing Materials

Effects of Electroactive Crystal Phases and Porous Structure on Triboeletrication of Poly(Vinylidene Fluoride)

Why 1.5-Nanometer Titanates and Zirconates Are Better Than Silanes

The Effect of Hygrothermal Exposure on the Thermal Conductivity and Density of Nanocellulose Based Foams

Phenolic Foams with the Re-Entrant Porous Structure: Fabrication, Structure and Properties

Ultrafast Removal of Pathogens from Wastewater Using Acid-Base Foams

MARCH 18 Tuesday PM

BRULE ROOM, 2:00-5:30 PM

TITLE

Effects of N2 and CO2 as Physical Blowing Agents on the Foamability of Linear and Branched PA6

In-Situ Visualization of Crystal Nucleation and Growth Behaviors of Polypropylene (PP) Under High Pressure CO2

Solubility and diffusivity of CO2 and N2 in TPU and their effects on cell nucleation in batch foaming

Engineered Nanofibers with Enhanced Foamability of Linear Polymer

The Effects of Material Properties on Microcellular Injection Molding Simulation

Crystallization and Elasticity Behavior of Poly(ether-block-amide) (Pebax®) Foams Manufactured by High-Pressure Foam Injection Molding with Mold Opening under N2

Optimizing Process Condition of PU Chemical Foaming: Validation of Material Properties for Numerical Simulation

ANTEC® 2019 PROGRAM IN THERMOPLASTIC MATERIALS & FOAMS DIVISION

MARCH 19 Wednesday AM

FOAM EXTRUSION AND INJECTION MOLDING

TITLE

Role of Polyamide 6 as the Antishrinkage Agent in PA 6/PEBAX Blends

Stepped Isothermal Method and Stress Rate Accelerated Creep Rupture Tests for Efficient Creep Investigation of Engineering Thermoplastics

Challenge to Prepare for Flame-Retardant Polypropylene Foam Boards

Modeling of a Foamable Mixture Flow through a Heat Exchanger and Relation to Foam Inhomogeneities

Mechanical Properties of Extruded Polypropylene Foams

Thermoforming evaluation of Coextruded Multilayer EVOH/LDPE Film/Foam

HIGHLIGHTS FOR TPM&F BOARD MEETING

Meeting Date: September 12, 2018
6:30PM Eastern Time Montreal, QC

ATTENDANCE

Attending the BOD meeting in person: Xiaoxi Wang, Gary Wilkes, Max Wingert, Stéphane Costeux, Miguel Perez, Anson Wong, Jim Throne, Daniel Marginson, Stephane Costeux. **Attendence by phone:** *Theresa Healy, Kim McLoughlin, N.S. Ramesh, Aaron Guan, Perry Vadhar, Sal Monte, Chad Zeng.*

SECRETARY REPORT – THERESA HEALY

The last BOD meeting minutes that were held on May 09 were distributed on June 22, 2018 via email and they were posted to The Chain. I have attached them to this report wince they need to be voted on and approved. Xiaoxi made a motion to approve the minutes and Max seconded. BOD meeting minutes are now approved.

CHAIR REPORT – XIAOXI WANG

Xiaoxi thanked the committee members for all the excellent work involved with the FOAMS® 2018. Xiaoxi mentioned that the Chair Elect for 2020 will be Chad Zeng. Donna is working on the Polyolefins Conference which is already in the planning stages. There were also kind words said in honor of Ray Shute's passing. We will all miss him. Donna will assume the responsibility of Nomination Chair. There will be a $500 scholarship awarded in his honor. Xiaoxi will coordinate with Kim and the Education Team for more details.

COUNCILOR REPORT – PERRY VADHAR

Next Council meeting is on Sept. 22, 2018, in Charleston, SC. Effective October 1, 2018, all SPE Chapters (US Sections and Divisions) in good standing will be eligible for enrollment in the SPE Chapter Insurance Program. The new program provides Chapters with important insurance safeguards including:

- General Liability
- Directors & Officers Liability
- Employment Practice Liability
- Fidelity (Employee/Volunteer Dishonesty)

The annual premium for the Commercial General Liability policy is currently $200. The annual premium for the Management Liability policy is currently $250. Each Chapter is responsible for their $450 annual premium.

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All the current details of this program are found at www.4spe.org/ChapterInsurance. Perry will share more details.

Operating Policy Number 013 & 014

SECTION & DIVISION ESTABLISHMENT AND ONGOING REQUIREMENTS. Changed the position of Membership Chair to a required position (not "or") due to needing that position for automatic reporting with the new membership system. Technical Program Chair is not mandatory as that was the "or" position with Membership Chair. This occurs in several places.

MEMBERSHIP REPORT – ANSON WONG

Committee Members: Anson Wong (Chair), Dale Grove, Kimberly Mcloughlin, Aaron Guan, Raymond Shute.

Membership Trends

	09/2018	04/2018	Difference
Professional	484	514	-30
Young Professional	39	36	+3
Student*	41	66	-25
Emeritus	33	34	-1
Distinguished	1	1	0
Total	593	651	-52

* Including 6 being added by SPE as part of our free student membership initiative. Total membership decreased by -21 compared to one year ago (09/2017).

I. SPE Membership System

Goal: Assess and work with SPE to improve its membership reporting system to help us design membership growth, and to improve our book-keeping on membership data.

- The new membership system *(May 2018)* allows you to download up-to-date membership list in the TPM&F Division, with detail information *(contact info, type of membership, and join/renew/expiry date)*
- The system seems stable *(no technical issue)* so far
- Potential areas of improvement
  - Membership trend vs. time information is still not available *(as the current setup provides a snapshot)*
  - SPE-wide membership summary *(e.g., membership by division, geography)* is no longer available
  - SPE has been contacted to understand if these functionalities could be restored / added

II. New Membership Growth

- Goal: To attract new members from different groups and geography
- Student Members
  - Continued our free membership initiative for student attendees of TPM&F sponsored conferences. SPE has been contacted to add qualified student participants in ANTEC® 2018 to TPM&F division *(only 7 qualified, and within that 6 are new TPM&F members)*. Many TPM&F student presenters are from USA *(therefore already covered by PLASTICS)*.
  - We will do the same for qualified student participants in FOAMS® 2018.
- Recruit SPE E-members – Email contacts does not seem to be effective.

ANTEC® 2019 REPORT – CHAD ZENG/GARY WILKES

- Meeting is March 18-21 in Detroit, this a about 1.5 month earlier than the usual meeting time in early May.
- SPE is restructuring the strategy of ANTEC®. Among the 4 days, there will be 2.5 days for technical program, and the other 1.5 days will be for commercial activities. There will be only 14 rooms, a simple math tell us that there are altogether 35 technical sessions, even slight fewer than ANTEC® 2018, which has 36 session. Realistically we may have 3 session at most.
- Because of the early meeting time, everything has to be done earlier, paper submission deadline is October 19, about a month away. Paper should be submitted through www.4spe.org/ANTEC®. You need to register first before submission even you have submitted paper in previous ANTEC®. Review needs to be done by November 14, and final revision needs to be completed by December 1. Preliminarily program will be published on line by December 8 and be included in January issue of PE magazine. Chas will need volunteers for reviewing the submissions.

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- Chad raised the issue once again on the format of submission due to recent changes by many journal publishers on copyrights and what they consider for duplicate submission. He strongly suggested allowing for PPT slides in lieu of the typical five page manuscripts. The message was relayed to SPE and we are awaiting instruction.

FOAMS® CONFERENCE COMMITTEE – STEPHANE COSTEUX *(See page 11 in this newsletter)*

EDUCATION CHAIR – KIM MCLOUGHLIN

Committee Members: Dale Grove, Perry Vadhar, N.S. Ramesh, Ray Schute, Anson Wong.

Reedy Scholarship Winners Selected

- Two students selected, both students presenting at FOAMS® & will be reimbursed $500 each.
- Number of applications was low (4) despite multiple email invitations sent directly to students and professors who were planning to present.
- Anticipated quality of presentations is very high, and topics are relevant to TPM&F.
- Winners are already making significant contributions and are on track to be leaders in our field.
- *Once the awards are announced, we would like to obtain a short bio and a photo of each student for our newsletter.*

Salvatore J. Monte 2018 Scholarship Awarded

Awarded to Forest Baker, mechanical engineering undergraduate student at Kettering: recognized leader with academic, professional, and community experiences in plastics engineering.

- Need to attract more applicants next year:
  - Create email list of professors, targeting schools that attract undergraduate plastics engineers.
  - Contact past winners to ask how they learned about the scholarship and to ask them for help spreading the word.

U of Toronto Student "Plastics & Sustainability" Papers Written

- SPE Student Chapter at U of Toronto created a contest for papers on the topic of Plastics & Sustainability
- High quality, thoughtful, papers developed after multiple rounds of writing and judging as well as recruitment of U of T professors as advisors.
- Winners selected and published in our TPM&F Newsletter. Monetary prizes awarded.
- What other publications might want to publish these articles?

2018 TPM&F Education Initiatives

SPONSORSHIP	2018 AMOUNT	TARGET	STATUS
SALVATORE J. MONTE SCHOLARSHIP	$4000	UNDERGRADUATE PLASTICS ENGR. STUDENT	AWARDED
SPE STUDENT ACTIVITIES FEE	$2500	ANTEC® STUDENT ATTENDEES	DONE
CHATTERJEE TRAVEL AWARDS	2 @ $750	CONF. PRESENTER (GRAD. STUDENT)	AWARDED ANTEC®
REEDY SCHOLARSHIP	2 @ $500	CONF. PRESENTER (GRAD. STUDENT)	SELECTED FOAMS®
PLASTIVAN	$1750	PRE-COLLEGE STUDENTS & TEACHERS	IN-PROCESS

TREASURER'S REPORT – MAXWELL WINGERT

Financial Summary: Fiscal Year 2017-18 ending division balance is $219,652.47, down by $5,541.54 from the previous year end balance of $225,194.01. We missed out on PO 2018 income on this report because the check came later than normal (the TPM&F proceeds were $14,281.15).

- The loss is less than was budgeted for, due to the financial successes of our investment account and because the following categories were more than 50% underspent:
  - Best Paper Awards
  - Non-ANTEC® Board meetings
  - Outstanding Achievement Award
  - Student Membership Subsidy

    We only paid SPE for the student membership subsidy once and I believe this was all based on FOAMS® 2017 attendees

The total income was $20,358.64; the total expenses were $25,900.18.

The FY18-19 proposed budget is shown below. We will vote on this budget at the board meeting.

Investment Account Update: Between July 1, 2017 and June 30, 2018, the Wells Fargo Advisors account managed gained 6.2% from $157,838.19 to $167,638.64. We were charged the traditional 0.21% quarterly fees (a total of $1,394).

WITH FONDEST MEMORIES . . .

William (Bill) Carteaux, the longtime president and CEO of the Plastics Industry Association, the largest plastics association in North America, died on Dec. 10 after a battle with leukemia at the age of 59. His family writes in the Dec. 10 post to Facebook: "To say we are heartbroken, crushed and just devastated is such a grand understatement. We have all lost such a wonderful human being who deserved to be in this world for so much longer than he was. Our loss is great, and the void is immeasurable. He was a true soulmate and husband, a proud father, a blessed father-in-law, a beloved grandfather, treasured brother, adored friend and revered leader." We are deeply saddened by this news. Our thoughts and prayers goes out to his family.

Prior to becoming PLASTICS president and CEO in February 2005, Bill Carteaux spent more than 20 years in the manufacturing sector. He came to PLASTICS from Demag Plastics Group, where he was president and chief executive officer. Carteaux previously served as the company's executive vice president. Prior to joining Demag, he spent eight years with Autojectors, a manufacturer of vertical injection molding machines, as its president.

Our own SPE TPM&F board member, Raymond Joseph Shute, Jr., 67, of Olathe, passed away on August 22, 2018 at Olathe Medical Center.

Raymond was a Chemist by trade, and worked in the chemical and foams industry for over 46 years. He was recognized by his peers and colleagues as an expert in his field, holding several patents, and enjoyed mentoring, training, and helping the development of his fellow chemists and scientists. Beyond serving as board director of our division, he was also a member in the Society of Automotive Engineers, American Society of Testing and Materials, as well as the American Chemical Society. He was invited and provided many technical presentations at society conferences. He also held positions on the Board of Directors for the American Chemical Society regional and national chapters, and a variety of leadership positions with the Society of Plastics Engineers.

Raymond is survived by his loving wife, Anka, his son, Raymond Shute, daughter-in-law Christine, and grandchildren Abigail, and Cameron. Sister, Susan Vasselli (Shute), and husband Joseph Vasselli, niece and nephew James and Veronica (Zemon). Sister-in-law Monica Boynton, and husband Gerry Boynton, niece and nephew Heather and Ryan. Our thoughts and prayers goes out to his family.

IMPROVEMENT IN MORPHOLOGY AND MECHANICAL PROPERTIES OF EXTRUDED POLYSTYRENE FOAMS WITH TRISAMIDE BASED ADDITIVES

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Abstract

Polystyrene (PS) is a low-priced, amorphous polymer, showing excellent foaming behavior. Thus, PS foams are widely used in variety of applications such as building and construction where a considerable mechanical strength is required. To address this, in this study,1,3,5-benzene-trisamides are used as a novel nucleating agent (NA) for PS foams. The NAs can be dissolved in PS melt at the certain concentration and processing temperature. The dissolved NAs can crystallize upon cooling in finely dispersed, one-dimensional, highly ordered nano-fibrillar objects. Self-assembly of these nano-fibrils into three-dimensional objects, which act as nucleating sites for the foam cells, takes place. We obtained PS foams with 0.1, 0.2 and 0.5 wt% of BTA using tandem foam extruder. Neat PS foams were also produced in a same way as a reference. With 0.2 wt% BTA, 35 times cell size reduction (18 µm) and 70 % reinforcement in compressive modulus compared to neat PS foams was achieved.

Introduction

PS foams have been mainly applied as insulation panels or roofs for building and construction. They are also used in packaging and cushion core for crush helmet and surfboard, where the materials are required to absorb high energy or to be resistant to external impact. For such applications, PS foams should exhibit a sufficient compressive modulus (typically in the range of 7.4 to 25 MPa [1]) to meet the requirements. The mechanical properties of the PS foams are strongly influenced by foam density as well as a variety of other factors, including intrinsic reinforcing effect of additives, orientation of fibrillar additives, cell opening effect, gas pressure inside of the closed-cell foams.

There have been numerous researches conducted to enhance the morphology and/or mechanical properties of PS by insoluble additives such as talc, thermally reduced graphite oxide, [2] expanded graphite, [3] multi-walled carbon nano tubes, [4],[2] carbon nano fibers and activated carbon particles. [3] However, common problem of using insoluble additives was an agglomeration which could cause a non-uniform additive dispersion and therefore, inhomogeneous cell size distribution as well as deteriorated mechanical properties.

To address this problem, recently a new generation supramolecular additives namely, 1,3,5-benzene-trisamide based NAs, have gained a significant attention. Depending on the temperature and concentration, the NAs can be dissolved in PS melt and are able to self-assembly upon cooling, in which molecule stacks are connected by secondary non-covalent bonds, such as hydrogen bonds and $\pi - \pi$ interaction. [5], [6] Molecule stacks build up into fibers in micrometer scale providing large surface areas for foam cell nucleation without agglomeration. There are several studies available in the literature showing the reinforcing effect of 1,3,5-benzene-trisamide based NAs on the compression properties of i-PP foams. Stumpf et al. [7] have shown the conceptual approach of foam injection molding of isotactic polypropylene (i-PP) with supramolecular additives for the first time. They achieved improvement in mechanical properties of i-PP foams with the introduction of 0.02 wt% NAs. Another study based on 1,3,5-benzene-trisamide based NAs as reinforcement agents for i-PP was exhibited by Mörl et al. [8] The researchers achieved extruded i-PP foams with improved morphology and 100% better compression modulus in the presence of NAs than the those of the neat i-PP. Additionally, it was claimed that the presence of the supramolecular fibers on cell walls enhanced the compressive modulus. These researches show the great potential of supramolecular additives acting as nucleating agents with additional reinforcing effects in different foaming processes.

The goal of this paper is to transfer the concept of using commercially available 1,3,5-benzene-trisamide-based NAs as a foam nucleating and reinforcing agent. By this way, it was aimed to improve mechanical properties of extruded PS foams for various applications.

Materials

Amorphous PS (Styrolution PS168 N, Melt volume-flow rate (200°C, 5 kg): 1.5 cm^3/(10 min) according to ISO 1133) was purchased from INEOS STYROLUTION. Chemical used as nucleating agent for PS, as illustrated in Figure 1, was commercially available nucleating agent (N,N',N''-1,3,5-benzenetriyltris(2,2-

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dimethylpropanamide)) Irgaclear XT386, BASF SE). Supercritical carbon dioxide (CO_2) with a purity of 99.9 % with less than 5 vpm moisture was directly used as a blowing agent. Ethanol was applied as a co-blowing agent to further enhance the plasticization and decrease the foam density. [2]

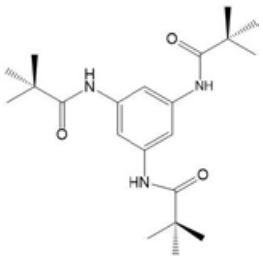

Figure 1. Chemical structure of the benzenetrisamide-based NA

Sample Preparation

PS foams were manufactured by using a technical scale tandem foam extrusion line from Dr. Collin GmbH (Twin screw extruder with 25 mm screw diameter and L/D of 42; single screw extruder with 45 mm screw diameter and L/D of 30) equipped with a slit die with a 0.6 mm gap in one step. PS foams with three different concentrations (0.1 wt%, 0.2 wt% and 0.5 wt%) of trisamide-based NAs were produced. The neat PS foam samples were prepared in a same way as a reference material. The detailed conceptual approach of the foam extrusion was described in the previous study [8]. The processing parameters, used for the foam extrusion of 1,3,5-benzene trisamide-based PBT, are tabulated in Table 1.

Table 1. Processing parameters for foam extrusion process

Melt temp., °C	**Die temp., °C**	**Screw speed, rpm**	**CO_2/EtOH, wt% / wt%**
113-118	126	8	4/3

Characterization

The water displacement method (ISO 1183) on a Mettler Toledo electric balance with a density kit was used to measure the bulk densities of foam samples. A minimum of three measurements for each concentration of foam were recorded. The average of the recorded values was determined. Individual cell diameters were determined by manually on the scanning electron microscopy (SEM) (Jeol JSM-6510) micrographs using a public domain software ImageJ. All SEM micrographs were obtained out of the foam samples which were cryo-fractured in liquid nitrogen and sputter coated. Compressive moduli of extruded PS foams were measured by a Universal Test Machine (Zwick Roell Z050) based on the test standard DIN 53421. Samples for compression test were prepared by cutting foams into cylinders with 10 mm diameter and 10 mm length. The compressive loads were applied perpendicularly to the extrusion direction of the foam samples. The compression strain was limited to 30%, which was sufficient to characterize the modulus and plateau stress values for each specimen.

Results and Discussion

The foam morphologies of the neat PS, PS with 0.1 wt%, 0.2 wt% and 0.5 wt% NAs are depicted in Figure 2.

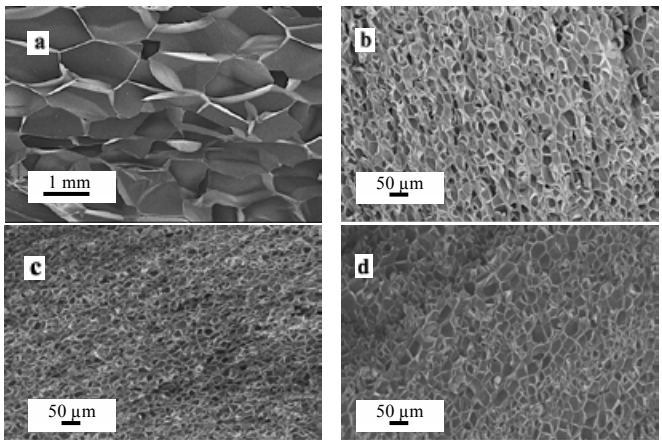

Figure 2. SEM images of neat PS (a), PS + 0.1 wt% (b), PS + 0.2 wt% (c), PS + 0.5 wt% (d)

As it can be seen from Figure 2, there is a significant improvement in foam morphology with the introduction of NAs independent from the concentration in comparison with the neat PS. Trisamide based NAs led to at least 20 times cell size reduction and 4-5 orders of magnitude increase in cell density. It was observed that with increasing NAs concentration from 0.1 wt% to 0.2 wt% cell size decreased from 26 $\pm$ 7 µm to 18 $\pm$ 6 µm. Nevertheless, further increase in NA concentration did not provide further decrease in cell size. PS foams with 0.5 wt% NA led to foams with mean cell size of 31 $\pm$ 6 µm which is even higher than those of 0.1 wt% NA. Similar behavior was observed with the foam densities of the PS foams having different concentrations of NAs. Increase in NA concentration from 0.1 wt% to 0.2 wt% led to increase in foam density from 73 $\pm$ 1 kg/m^3 to 77 $\pm$ 1 kg/m^3. Foams with 0.5 wt% NA exhibited lower density of 69 $\pm$ 1 kg/m^3 where the neat PS reached the lowest density of 52 $\pm$ 1 kg/m^3 with the highest mean cell size of 632 $\pm$ 182 µm. The mean cell size and foam density results show that the change cell size also corresponds to the change in foam density depending on the NA concentrations. The unexpected increase in cell size and decrease in foam density from 0.2 wt% to 0.5 wt% NA can be explained by incomplete solubility of the NA in PS at 260 °C. Therefore,

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0.2 wt% NA was found as the limit for solubility in this study. When NA concentration reaches to 0.5 wt%, partly insoluble NA might exist in a form of agglomerates lowering the nucleation efficiency and leading to the foams having larger cells and inhomogeneous cell size distribution (Fig. 2d). Foam densities, mean cell sizes and cell densities of the neat PS, PS with various concentrations of NAs are summarized in Table 2.

Table 2. Foam density, mean cell size and cell density of extruded PS foams

	Foam density, kg/m^3	**Cell size, µm**	**Cell density, cells/cm^3**
Neat PS	52 ± 1	632 ± 182	2.7 x 10^3
PS+0.1 wt% NA	73 ± 0.5	26 ± 7	5.6 x 10^7
PS+0.2 wt% NA	77 ± 1	18 ± 6	1.5 x 10^7
PS+0.5 wt% NA	69 ± 1	31 ± 10	3.1 x 10^7

It is well known from the Gibson-Ashby model that foam density plays a significant role on the compressive modulus [9]. Increase in foam density means higher fraction of solid matrix in foams, both cell walls and cell struts. According to the model, there are three components contributing to the stiffness of a closed-cell. The first component is cell struts / cell wall edge bending stiffness, which determines the elastic modulus. The second component is cell wall elastic buckling, which contributes to elastic collapse. The final component is the internal gas pressure of the closed cells, which is negligible. The summation of the first two components can be expressed with Equation 1:

$$\frac{E_f}{E_s} = \phi^2 \left(\frac{\rho_f}{\rho_s}\right)^2 + (1-\phi)\frac{\rho_f}{\rho_s} \qquad (1)$$

E_f is the elastic modulus of the foam; E_s is the elastic modulus of the solid material; ρ_f is the foam density; ρ_s is the solid polymer density; Φ is fraction of polymer contained in cell struts, and 1- Φ is therefore the solid fraction in cell walls.

As it was already explained by the cubic cell model, the foams with 0.2 wt% NA having the highest density of 77 ± 1 kg/m^3 exhibited the highest compression modulus of 47.9 ± 3 MPa. 0.2 wt% NA led to 70% increase in compression modulus compared to those of neat PS (13.8 ± 2 MPa).

In order to analyze the effect of NA on the mechanical properties of the PS foams independent from foam density, the specific modulus of the foams was calculated by dividing the foam densities to the compression modulus. The specific moduli of the PS foams as a function of additive concentration are shown in Figure 3.

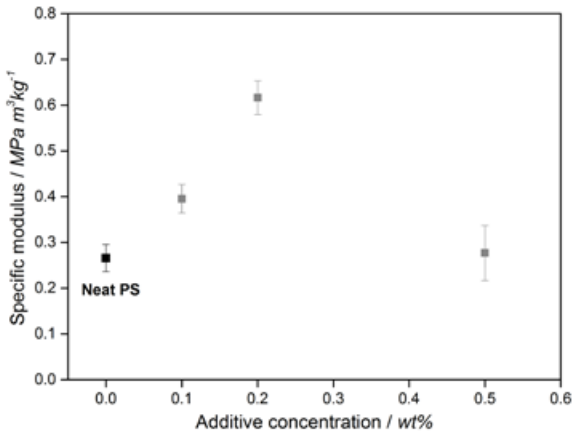

Figure 3. Specific moduli of PS foams with changing additive concentration

As it can be seen from Figure 3, the neat PS and PS with 0.5 wt% NA possessed the lowest specific modulus of 0.39 ± 0.03 and 0.27±0.06 MPa m^3 kg^{-1}, respectively. For foams with 0.1 wt% and 0.2 wt% NA, the compression moduli increased with increasing NA concentration. 0.2 wt% NA exhibited the highest compression modulus of 0.62 ± 0.03 MPa m^3 kg^{-1} which is 125% higher than the those of the neat PS. It is well known in the literature that mechanical properties of the foams are not directly affected by the morphology including cell size and cell density. Therefore, we attribute the increase in modulus to the presence of nano-fibrillar structures having a high aspect ratio. These nano-objects are beneficial for stress transfer from the polymer to the additives and provides additional reinforcing effect to the foam. A similar reinforcing effect of BTA fibers on compressive mechanical properties has been already shown for i-PP by Mörl et al. [8] The reason of decreased compression modulus with the introduction of 0.5 wt% NA would be due to the incomplete solubility of the NA in PS melt. Non-dissolved NA agglomerates might act as defecst in the foam, leading to deteriorated compression properties and maybe premature failure of the material.

Conclusions

Neat and 1,3,5-benzene-trisamide-based NAs nucleated PS foams were produced by tandem foam extrusion line. NA was soluble in PS and these dissolved NA molecules crystallized into nano-fibrillar objects with high aspect ratio. It was found that the solubility of NA at 260 °C in PS is limited and determines the nucleation efficiency. Thus, while the 0.2 wt% NA led to foams with the smallest cell size (18 ± 6 µm), which was 35 times smaller than those of the neat PS, further addition of NA up to 0.5 wt% did not reduce foam cell size (31 ± 10 µm), which is due to the incomplete solubility of NA. Due to the

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higher foam density which was resulted from cell size reduction, foams with 0.2 wt% NA exhibited the best mechanical performance. Compared to the neat PS 70 % reinforcement in compressive modulus was achieved with 0.2 wt% NA. The specific modulus results showed that the nano-fibrillar NA structures on the cell walls and cell struts attributed to the further reinforcement in compressive modulus of PS foams.

References

[1] Technical Data Sheet of Product Celfort® 300 & Foamular® 400,600,1000 Insulation Boards, http://www2.owenscorning.com/worldwide/admin/tempupload/pdf.2-74495-157_HighDensBro_E.pdf (Accessed in June 2018).

[2] C. Okolieocha, T. Köppl, S. Kerling, F. J. Tölle, A. Fathi, R. Mülhaupt, and V. Altstaedt, *J. Cell. Plast.*, **51**, 413–426 (2015).

[3] C. Zhang, B. Zhu, and L. J. Lee, *Polymer*, **52**, 1847–1855 (2011).

[4] P. Gong, P. Buahom, M.-P. Tran, M. Saniei, C. B. Park, P. Pötschke, *Carbon N. Y.*, **93**, 819–829 (2015).

[5] T. F. A. De Greef and E. W. Meijer, *Nature*, **453**, 171–173 (2008).

[6] E. W. De Greef, F.A., Smulders, M.J., Wolffs, M., Schenning, A.P..H.J., Sijbesma, R.P., Meijers, *Chem. Rev.*, **109**, 5687–5754 (2009).

[7] M. Stumpf, A. Spörrer, Schmidt, H.-W., and V. Altstädt, *J. Cell. Plast.*, **47**, 519–534 (2011).

[8] M. Mörl, C. Steinlein, K. Kreger, H.-W. Schmidt, and V. Altstädt, *J. Cell. Plast.*, **0**, 1–16 (2017).

[9] L. J. Gibson, M. F. Ashby, *Cambridge Solid State Science Series*, 2nd Edition (1997)

FOAMS® CONFERENCE REPORT

Stéphan Costeux

Summary of the status of FOAMS® 2018 as of Sept 9, 2018.

TECHNICAL PROGRAM:

27 speakers *(incl. 3 keynotes)* from 10 countries

12 from Industry

14 from academia

1 national lab

5 posters in competition

TUTORIAL:

Tutorial only	10
Tutorial w/ conference	33
Total Tutorial:	43

CONFERENCE:

Speaker/BOD/Plenary	27
Student presenters	12
Full conference (Pro)	46
Banquet only	2
Exhibitors	2
Total Conference:	89

Current revenue from registration: 45,870 USD

About 2,500 USD from exhibitors / sponsors

Heard comments from several companies that they spent their budget on NPE this year, and were not able to sponsor or send attendees. Also, very few local students or professors from Quebec.

Expenses will be determined right after the conference. A small profit is expected for TPM&F and the Quebec Section is expenses are as planned.

NEXT CONFERENCE: FOAMS® 2019

September 16-20, 2019 in Valladolid, Spain. Main venue will be the University of Valladolid, located in the city center. Nice facility for conference.
Valladolid is 1 hour from Madrid by high speed train. Several very nice hotels at very affordable price.

The foam laboratory is a few kilometers away, can arrange a bus for lab tour with foam demo. Likely tutorial on 17-18 Sept. and conference on 19-20 Sept. Can also start on 16 Sept. Final decision during BOD meeting.

PROTECTED BIOFILM GROWTH IN MACROPOROUS POLYVINYLIDENE FLUORIDE CARRIERS FOR BIOLOGICAL ORGANIC REMOVAL FROM MUNICIPAL WASTEWATER

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Abstract

Attached growth bioreactor process provides surface area to support the growth and attachment of bacteria, and thereby a means to biologically remove organics from wastewater. In this work, open-cellular polyvinylidene fluoride (PVDF) foams consisted of macroporous structures were designed and fabricated to promote the efficiency of existing biofilm carriers for wastewater treatment. A manufacturing approach that integrated compression molding and particulate leaching was employed to fabricate the PVDF foams. Different contents of salt were used as leaching agent to fabricate PVDF foams with macroporous structures of different total protected surface areas. Experimental studies were conducted to elucidate the structure-to-performance relationships of these macroporous PVDF carriers in terms of bacteria-to-carrier interaction and organic removal efficiency.

Introduction

About 70% of earth surface is covered by water; however, less than 0.01% of this amount is reachable and useable for humans. Furthermore, climatic variation, industrialization, and urbanization have also put this small portion of freshwater in danger. Surveys show that 30% of all diseases worldwide are caused by polluted water [1]. Due to the shortage of clean water resources, providing clean water for drinking, agriculture, and industry has become a crucial challenge. In this context, wastewater treatment has been the focal point among scholars to address this challenge in recent decades.

Wastewater treatment processes can be subdivided into three methods: physical, chemical and biological processes. For the treatment of large area conventional treatment units are used; however, construction of treatment units is not economical for smaller areas. Biological treatment processes in small bioreactors play a significant role to reduces both operational and maintenance costs [2]. In these processes, microorganisms convert suspended and dissolved organic matters into cell tissues and various gases. Cell tissues have higher density than the suspended phase and will be settled to the bottom of the reactor, and thereby purifying water. Biological treatment processes can further be subdivided into suspended growth technology and attached growth systems. In suspended growth technology, the omnipresence of microorganisms leads to biodegradation of pollutants in the wastewater. In attached growth systems, support media are suspended in the wastewater, providing surfaces to which microorganisms can adhere. This eventually develops into biofilm, which consists of microorganisms and high molecular weight natural polymers (i.e., extracellular polymeric substances (EPSs)) that the microorganisms produced [3]. Excessive accumulation of microorganisms in the biofilm increases biomass concentration, which enhance the organic removal efficiency in attached growth systems over the suspended growth.

Designing support media has a significant impact on the biofilm formation in attached growth systems. The type of material, surface area, surface roughness, and porosity of media are the most important factors to be considered in their design. Rough surfaces and porous materials would provide larger specific surface areas on which microorganisms can adhere [3-5]. Shear forces are low near rough surfaces and inside pores. Therefore, such structures would help protect microbial cells and increase their adhesion to these surfaces. This eventually promote the formation of biofilm.

Moving bed bioreactor (MBBR) is a well-established technology that uses attached growth systems in wastewater treatment [6]. In MBBRs, carriers are used as biofilm supporters. Moving bed biofilm carriers could significantly increase the organic removal efficiency of MBBRs due to their large specific surface areas. Their low density also facilitates their movement inside the bioreactor [7]. However, one of the major drawbacks of media in the MBBR is that at high organic loads the biofilm attached to the media cannot sustain high shear forces and would be detached from the support media. To

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enhance promising features of MBBR's media and to diminish its limiting factors, this research aims to design and develop a novel biofilm carrier by using the open-cellular foam as protective structures to biofilm. An open-cellular foam is a substance consists of interconnected pores. Comparing to the existing biofilm carriers in the market such as glass, peat, powdered minerals, expanded clay, and polyurethane foam cubes [8], open cellular foams have remarkably larger specific surface area, higher porosity, higher surface roughness, lower density and higher adherence of biofilm to their surfaces [2]. These special properties of open cellular foams make them good candidates for biofilm generation in attached growth systems.

Experimental

Materials

Commercially available polyvinylidene fluoride (PVDF, Kynar 741, Arkema, with the molecular weight of 282 000 $g \cdot mol^{-1}$) was used to fabricate the porous biofilm carriers. Sodium chloride (NaCl, Windsor) and anhydrous sodium acetate (NaOAc, VWR) were used as leaching agents to produce the open-porous structures. All materials were used as received without further modification. Physical properties of materials are summarized in Table 1.

Table 1. Physical properties of PVDF, NaCl, and NaOAc

Materials	PVDF	NaCl	NaOAc
Melting Temp. (°C)	170	901	324
Density (g/cm^3)	1.78	2.16	1.53

Preparation of open-cellular PVDF biofilm carriers

PVDF powders were dry-blended with sieved NaCl or NaOAc particles with sizes ranging from 250 μm to 500 μm for NaCl and 106 μm to 250 μm for NaOAc. The PVDF-NaCl or PVDF-NaOAc mixtures, loaded with 80 wt.% or 90 wt.% of leaching agents, were molded by a compression molding machine (Craver Press, 4836 CH) into disc samples of 20 mm in diameters and 10 mm in thicknesses by the following procedures:

STEP 1. PVDF-leaching agent mixtures were loaded into a four-cavity mold and subsequently loaded into the compression molding machine with a preset temperature of 185°C.

STEP 2. The mold was maintained in contact with the top and bottom heating platens for 5 minutes without increasing the pressure to completely melt the PVDF.

STEP 3. Then samples and mold were pressurized to 5000 lbs-force for 5 minutes, and subsequently to 10 000 lbs-force for 10 minutes.

STEP 4. The mold was removed from the compression molding device and were loaded into a cooling module with circulating water for 10 minutes to cool down the molded samples.

STEP 5. Each sample was immersed in 500 mL of deionized water for 72 hours to leach out NaCl or NaOAc from the PVDF matrix. DI water was changed every 24 hours to avoid saturation of salt.

STEP 6. Samples were dried in an oven at 60°C for 24 hours.

Characterization of the open-celular structures of PVDF carriers

Foam morphology was characterized using scanning electron microscopy (SEM) (FEI Company, Quanta 3D FEG). The cross-sections of all samples were exposed by cryo-fracturing the samples under liquid nitrogen. The fractured surfaces were then sputter-coated with gold (Denton Vacuum, Desk V Sputter Coater). Open-cell content of each foam sample was analyzed by using a pycnometer (Quantachrome, Micro-Ultrapyc 1200e).

Analysis of the performance of open-cellular PVDF carriers

Three one-litre bottle bioreactors with 9.5 cm in diameters and 23 cm in heights were designed and implemented for testing the performance of open-cellular PVDF carriers for biofilm growth and biological wastewater treatment. A schematic of the setup is illustrated in Figure 1. Bioreactors were loaded with 48 samples of PVDF media prepared by using 80 wt.% or 90 wt.% of NaCl as well as those prepared by using 80 wt.% NaOAc. The suspended media filling ratio (i.e., volume occupied by carriers in the empty reactor) was 30 vol.%. In the initial setup, bioreactors were filled with 330 mL return activated sludge with 8385.4 mg/L volatile suspended solid (VSS), which was collected from Humber Wastewater Treatment Plant. Two air pumps with 6 outlet ports were used to supply oxygen to microorganisms in the bioreactors. Air pumps were connected to air stones to eliminate large air bubbles in the bioreactors, which would clog the tubes and are harmful to microorganisms' lives. Bioreactors were put in a digital orbital shaker with 170 rpm at room

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temperature. Bioreactors were fed by 300 mL high concentration feed with feed-to-microorganism ratio of 1. After 24 hours, 20 mL liquid samples were collected from the top segment of the bioreactors. The samples were put in a cold room at 4°C for further analysis. After collecting samples, the pumps and shaker were turned off for 2 hours for biomass settlement. Consequently, 300 mL clean water at the top segment of the bioreactors were replaced by 300 mL of fresh feed. The same processes were repeated daily for 76 days. For the first four days, organic load feeding had high chemical oxygen demand (COD) concentration to speed up biofilm formation in support media. Thereafter, the organic load concentration was decreased by a factor of 100 (i.e., 3 mL high concentration feed +297 mL deionized water). Table 2 summarizes the high concentration feed composition.

Table 2. Composition of high concentration feed

Component	Concentration (g/L DI Water)
CH_3COONa (NaOAc)	44.87
$NiCl_2{\cdot}6H_2O$	0.015
$CoCl_2{\cdot}6H_2O$	0.015
$CuCl_2$	0.04
$ZnCl_2$	0.025
$MnCl_2{\cdot}4H_2O$	0.25
$FeCl_2{\cdot}4H_2O$	0.15
$(NH_4)_6MO_7O_{24}{\cdot}4H_2O$	0.04
H_3BO_3	0.025
$MgSO_4{\cdot}7H_2O$	2.8
$CaCl_2{\cdot}2H_2O$	1.33

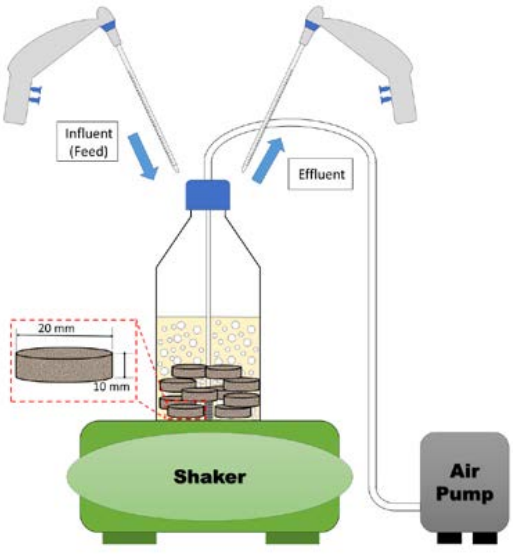

Figure 1. Schematic of bioreactor setup

Soluble chemical oxygen demand (SCOD) shows the capacity of wastewater to consume oxygen during the decomposition of organic matter. SCOD of the suspended phase in the bioreactors was measured as a representation of the organic materials inside the bioreactors. Samples were filtered by 0.45 µm syringe filter. 2 mL filtered samples were then injected into COD vials. Consequently, they were put in the digestor for 2 hours at 150 °C. After the digestion of COD vials, they were cooled to room temperature and SCOD was measured by COD analyzer (HACH, DR 3900). For measuring VSS, 5 mL of suspended phase sample was injected into a glass microfibre filter and an aluminum pan by the help of vacuum and was put in the oven at 105 °C for 2 hours. This mass was measured after cooling (m_1). Then the aluminum pan filter and the sample residue were put in a furnace at 550 °C for 20 minutes and their mass was measured after cooling (m_2). Equation 1 shows the calculation for VSS:

$$\mathrm{mgVSS/L} = \frac{m_{1\,(mg)} - m_{2\,(mg)}}{5_{(ml)}} \times 1000 \qquad (1)$$

Biofilm structure was characterized using environmental scanning electron microscopy (SEM) (FEI Company, Quanta 3D FEG). The cross-sections of samples were cut by a sharp blade. Biofilm detachment from the support media was tested by using sonicator (VWR company, symphony™).

Results and Discussion

Figure 2 shows that foams prepared by higher loadings of leaching agent led to higher open-cell contents or porosity. Moreover, PVDF-NaOAc foams have higher porosity comparing to PVDF-NaCl foams loaded with the same amount of leaching agent. Higher porosity of PVDF-NaOAc foams was caused by the higher volume fraction of NaOAc presented in the PVDF matrices.

Figure 3 shows SEM micrographs of 4 manufactured open-cellular foams. It can be seen that all four types of foams have large voids and high degree of interconnectivity among pores, which would provide large specific surface areas in these foams. Furthermore, Figure 2 shows that PVDF-NaCl foams consisted of well-defined pores with cubic structures. However, PVDF-NaOAc foams did not have regular pore geometries and the pores were less distinguishable.

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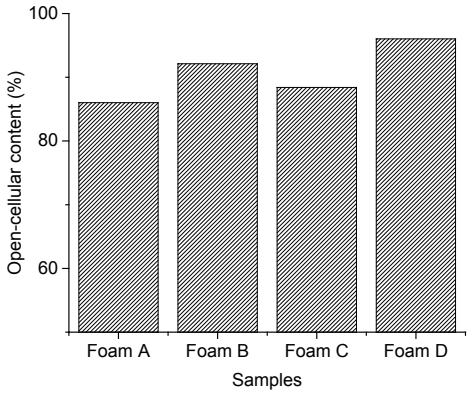

Figure 2. Open-cell content of PVDF-NaOAc/NaCl foams: (Foam A) 80 wt.% PVDF-NaCl (Foam B) 80 wt.% PVDF-NaCl (Foam C) 80 wt.% PVDF-NaOAc (Foam D) 90 wt.% PVDF-NaOAc.

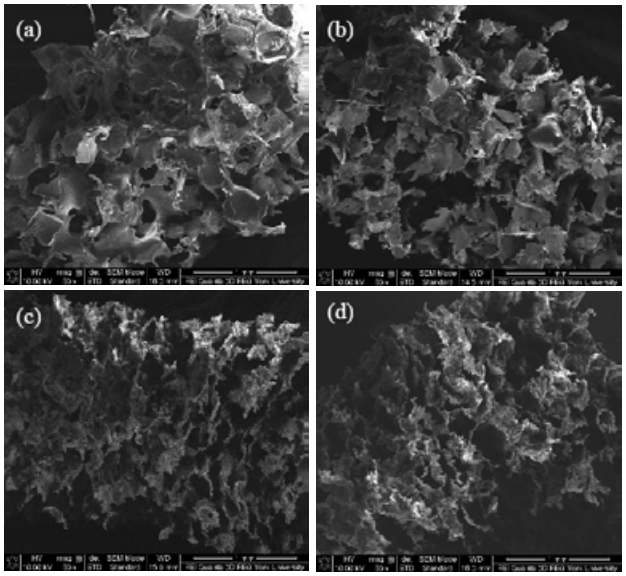

Figure 3. SEM images at 50x for (a), (b) 80wt%, 90wt% PVDF-NaCl (c), (d) 80wt%, 90wt% PVDF-NaOAc.

Structural strength, flexibility and fragility of the open-cellular foams depend different parameters. Leaching agent content and particle sizes of leaching agent are the two most important factors which affect the toughness and durability of the open-cellular foams. NaOAc particles were finer than NaCl particles, leading to higher fragility of PVDF-NaOAc foams. PVDF-NaOAc foams did not have enough strength to sustain the shear stress in the liquid phase and were completely damaged after 4 days being in the suspended phase. So, the bioreactor containing PVDF-NaOAc foams was stopped working. Due to the lower porosity of PVDF foams prepared by 80 wt.% NaCl than those prepared by 90 wt.% NaCl, the former had more strength. However, PVDF prepared by 90 wt.% NaCl were more flexible than those prepared by 90 wt.% NaCl and could be squeezed by a small amojnt of force. Figure 4 shows open-cellular foams before and after being used in the bioreactors. The images show that during 76 days of biological process, PVDF foams prepared by 90 wt.% NaCl samples were damaged due to the high shear stresses of the shaker and high retention time in the liquid phase. This defect in the PVDF foams prepared by 90 wt.% NaCl damaged the open cells inside the foam and decreased available surface areas for bacteria to attach and make biofilm. However, PVDF foams prepared by 80 wt.% NaOAc had stronger structures and retained their original shapes and cell structures during the experiment.

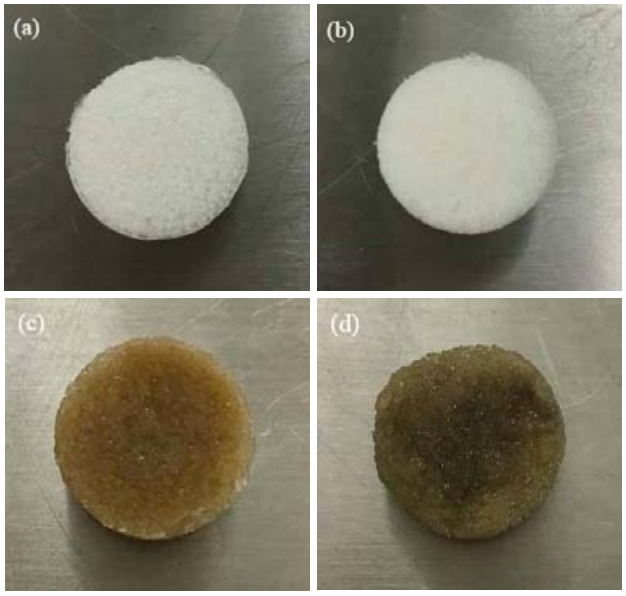

Figure 4. Open cellular foams before biological process(a), (b) 80wt%, 90wt% PVDF-NaCl, after biological process (c), (d) 80wt%, 90wt% PVDF-NaOAc.

Figure 5 shows SEM micrographs of biofilm attached to the support media. SEM images show that both all PVDF foams prepared by NaCl were successful in term of biofilm formation on their surfaces and their cross-sections. Existing biofilm on the media showed microorganisms' compatibility with new biofilm carriers. Moreover, the biofilm was seen at the core parts of the carriers which revealed the ability of bacteria to penetrate into the foams and make biofilm in all available surface areas. Moreover, SEM micrographs show that the cell sizes in the support media were large enough for bacteria to penetrate and make biofilm without clogging. Besides that, SEM images show higher biofilm aggregation and more regular structure of biofilm in the PVDF foams prepared by 80 wt.% NaCl than those prepared by 90 wt.% NaCl. This could be attributed to the damaged pores in the latter carriers.

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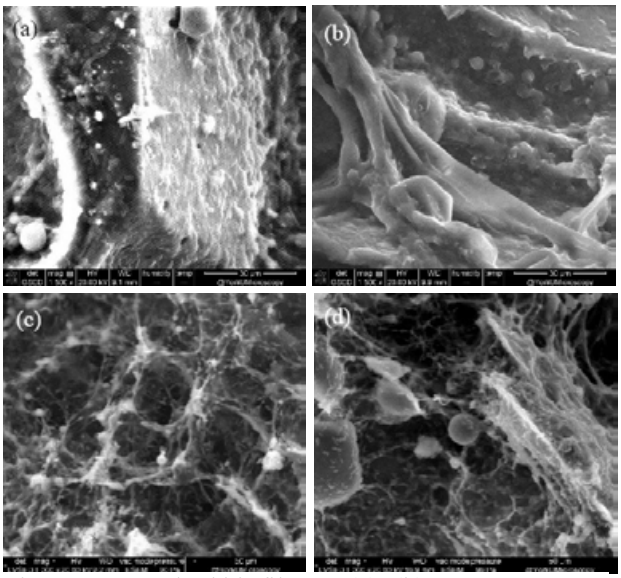

Figure 5. Attached biofilm on (a), (b) 80wt%, 90wt% PVDF-NaCl at 1500x (c), (d) 80wt%, 90wt% PVDF-NaCl at 1000x

Figure 6 shows the bioreactor containing PVDF foams prepared by 80 wt.% NaCl carriers had higher organic removal efficiency than that containing PVDF foams prepared by 90 wt.% NaCl. Although initial porosity of 90 wt.% PVDF-NaCl foam was higher than 80 wt.% PVDF-NaCl, well defined pores in the 80 wt.% PVDF-NaCl carriers during the experiment could build more biofilm on their surfaces which lead to higher organic removal efficiency of them compare to 90 wt.% PVDF-NaCl carriers.

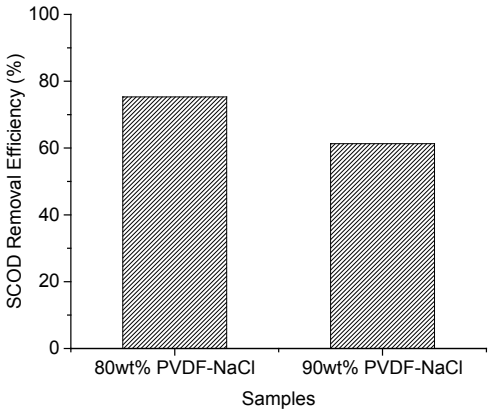

Figure 6. COD removal per gram of VSS for different bioreactors

Figure 7 shows the attachment efficiency of both media. This reduction in the VSS explains the microorganism's attachment to the media and biofilm formation. It can be seen that VSS reduction in 80 wt.% PVDF-NaCl carriers has higher slope than 90 wt.% PVDF-NaCl carriers, which shows better and faster functionality of 80 wt.% PVDF-NaCl carriers in biofilm formation.

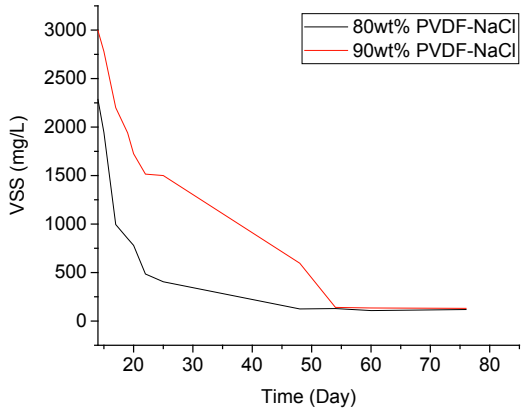

Figure 7. VSS change during the experiment

One sample of each 80 wt.% and 90 wt.% PVDF-NaCl carriers were put in sonicator device at room temperature for 20 h. The VSS detached from 80 wt.% and 90 wt.% PVDF-NaCl were 51.2 mg/L and 19.2 mg/L, respectively. The low amount of VSS detachment in both media confirmed their high ability in trapping microorganisms inside their pores.

Comparing 90 wt.% PVDF-NaCl carriers to the MBBR's media and other media in the literature, it can be shown that the removal efficacy that can be achieved using PVDF-NaCl carriers is 3 times higher in the TCOD removal and 2 times higher in maintaining the VSS attached to the carriers.

References

1. S. Sehar, I. NazP, *InTech*, (2016).
2. E. Loupasaki, E. Diamadopoulos, *Chemical Technology and Biotechnology*, **88**, (2012).
3. N. Qureshi, B.A. Annous, T.C. Ezeji, P. Karcher, and I.S. Maddox, *Microbial Cell Factories*, (2005).
4. S. Azizi, A. Valipour, and T. Sithebe, *The Scientific World Journal,* **2013**, (2013).
5. D. Garcia-gonzalo, D. García-gonzalo, and R. Pagán, *Postdoctoral Research,* (2015).
6. H. Ødegaard, B. Gisvold, and J. Strickland, *Water Science and Technology*, **41**, (2000).
7. C. Accinelli, M.L. Saccà, M. Mencarelli, and A. Vicari, *Bioresource Technology*, (2012).
8. S.G. Mosanenzadeh, H. E. Naguib, C. B. Park, and N. Atalla, *Applied Polymer Science*, **131**, (2014)
9. W. Moe, R.L. Irvine, *Environmental Engineering,* ,**826**, (2000).