SOCIETY OF PLASTICS ENGINEERS

Engineering Properties and Structure Division Newsletter

JANUARY/FEBRUARY 2015

CHAIRPERSON'S REPORT

Greetings Fellow EPSDIV Members!

It is hard to believe that 2014 has come to an end. It seems like only yesterday that I was shoveling myself out of a snowy northeast nightmare and now I find myself doing it again. It is times like these where I cannot but think of sunny Orlando, Florida and the ANTEC that is rapidly approaching. As always EPSDIV will be prominent, hosting 8 sessions, two of which are joint sessions with the Composites Group. We have heard your plea and as such have really focused on quality over quantity in 2015. We hope that you will be able to join us. Since ANTEC is being held during NPE, it is an opportune time to get out and meet all of the leading professionals in both industry and academia.

As promised, EPSDIV held its first quarterly seminar series on November 18th. Gayathri Sharma of PolyOne was kind enough to volunteer her time to teach all of us about the current research being conducted on thermally conductive polymers. It was a great talk on a very exciting new area of research. We wish to continue serving your needs; therefore, we're open to suggestions related to areas of research you would like covered in the future. If you have an idea, please email me. The Board will do its best to find leaders from industry and academia that are willing to share their latest work. As a reminder the seminars are free for all EPSDIV members and it is our way of saying thank you.

You may have noticed a survey in your inbox related to the value of your EPSDIV membership. I would like to thank those of you who have already responded and I encourage those that have not to please take a couple of minutes to help the Board better serve you. It is clear from those that have responded that we need to significantly improve our website. Daniel Schmidt has graciously volunteered to help us with this gigantic endeavor. The Board is currently working with SPE headquarters to update the EPSDIV website. It is our hope over time to build it into a database that provides exceptional value to you.

Again, if you have recommendations regarding what you would like to see on the website, please reach out to Daniel or myself.

It has been an exciting couple of months and I feel we have started making headway on providing value to your EPSDIV membership. As always, I am here to help and listen to your requests. Please take a second and contact me to let me know what you are thinking. Until then, I will see you in beautiful Orlando, Florida.

Jason Lyons

EPSDIV to Host 8 Sessions at ANTEC 2015

ANTEC 2015
MARCH 23-25, 2015
ORANGE COUNTY CONVENTION CENTER
ORLANDO, FLORIDA USA

NPE2015 THE INTERNATIONAL PLASTICS SHOWCASE
produced by spi

INSIDE THIS ISSUE

Board Member Nominees
(Please Vote for Five of the Following Six Candidates)

EMAIL your choice by **February 27, 2015**
to Luyi Sun at luyi.sun@uconn.edu

☐ **Sadhan C. Jana, PhD**

Dr. Sadhan C. Jana is currently a professor in the Department of Polymer Engineering at The University of Akron. He received a Ph.D. degree in chemical engineering from Northwestern University, worked at General Electric Corporate Research Center for four years, and joined the University of Akron in 1998. Dr. Jana served as chair of the Department of Polymer Engineering at the University of Akron from 2004 to 2011. He is the recipient of the National Science Foundation Faculty Early CAREER Award, Chemcon Distinguished Speaker Award, the Society of Plastics Engineers' (SPE) Fred E. Schwab Award for outstanding achievements in education, and Honorary Professorship from National University of Colombia, Bogota. He is a Fellow and Honored Service Member of SPE and serves on the boards of Engineering Properties and Structure and the New Technology Committee of SPE. He served in Engineering Properties and Structure Division as technical program chair, division award chair, and chair of the board. His term for senior senate status expires this year. Dr. Jana is also the chair of the SPE Education Award Committee. He is editor-in-chief of Springer Materials: Polymer Section and is an associate editor of Polymer Engineering & Science. In addition, he serves on the editorial boards of a number of peer-reviewed journals.

☐ **Hoang T. Pham, PhD**

Dr. Hoang T. Pham received his Ph.D in Polymer Science at The University of Akron. He is currently working at Avery Dennison with research interest in films for labels and specialty packaging. His current research interest includes special barrier, shrinkable, and sustainable films for packaging and labeling. Prior to that, Dr. Pham spent over 22 years at The Dow Chemical Company with a research and development focus on new materials and processing developments. Several key areas of focus are the structure property relationship modeling of polycarbonates and blends, acrylonitrile butadiene styrene copolymers, polyolefin and their blends leading to new products introduced to the market place for automotive, building construction, IT and communication housing, and packaging applications. Dr. Pham is also an active member of the Society of Plastic Engineers and has served on the Engineering Properties and Structure Division Board.

☐ **Sreekumar Pisharath, PhD**

Dr. Sreekumar Pisharath is a Senior Research Fellow with the Energetics Research Institute (EnRI) at the Nanyang Technological University (NTU), Singapore. He took his PhD in Materials Science and Engineering from NTU in 2005. Since then he has been associated with Energetics Research Institute (EnRI). His research interests are in the areas of synthesis and characterization of energetic polymers, thermal analysis of energetic material composites, deformation and fracture behavior and microscopy of composite materials. He has co-authored 12 research publications in peer reviewed journals including a book on energetic polymers published by Wiley-VCH. He is currently a Board member of EPSDIV and has been a professional member of SPE since 2010.

EPSDIV BALLOT (Continued)

☐ **Duane L. Simonson, PhD**

Dr. Duane L. Simonson obtained his Chemistry B.S. from the University of Wisconsin at River Falls, a M.S. from North Dakota State University, and a Ph.D. degree from the University of Virginia. After a NRC postdoctoral fellowship, he continued work at the Naval Research Laboratory in Washington, DC until 2014. Since March 2014 he has worked as a consultant with Research Support Instruments, Inc. His research interests include synthesis of sensor coatings, nanoparticles, polymers, and nanocomposites for protective and optical applications. Publications include papers, patents, and international invited, contributed, and keynote talks at chemistry, composites, and plastics industry and government meetings. His professional memberships include SPE, ACS, MRS, DEPS, SAMPE, and ASME.

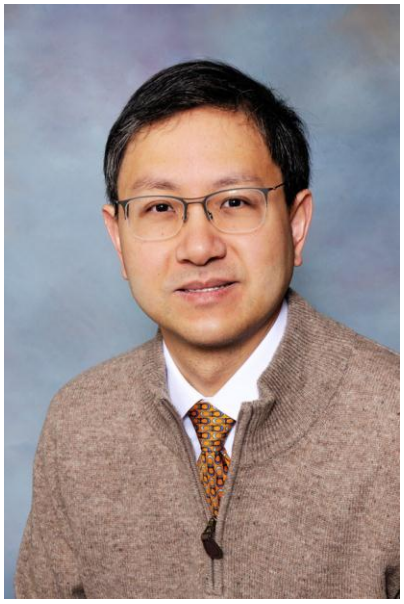
☐ **Brian G. Landes, PhD**

Dr. Brian Landes is a technology leader for The Dow Chemical Company in Midland, Michigan. For the past six years he has served as EPSDIV's Councilor. In this role he has worked to strengthen the ties between Divisions and Sections within SPE and develop strategies to attract new members to the Society. Dr. Landes also has served as SPE's Counselor Committee Chair for the past two years, learning how other divisions served their members and provided opportunities for their personal and professional development. Dr. Landes is passionate about developing outreach vehicles that can excite and rally community, students, and young professionals regarding opportunities in science and technology, SPE and EPSDIV. He is a SPE member that is interested in helping our Division and Society provide the highest value for SPE members.

☐ **Dick C. Bopp, PhD**

Dr. Bopp retired from NatureWorks LLC in Minnetonka, MN after working 18 years as a senior materials scientist where he worked on the development of Ingeo™ polylactide biopolymers. Prior to his position at NatureWorks, Dick worked at the General Electric Co. for 21 years. In 1992 he was the recipient of GE's Don Jaquiss Award for his development of a flame retarded, injection moldable Noryl resin for a McDonald's roof made from post-consumer recycled computer housings. In 1993 he was named Noryl Recycle Business Leader. Dick earned his bachelor's degree in chemistry from the State University of New York at Albany and his M.S. and Ph.D. degrees in polymer chemistry from Rensselaer Polytechnic Institute in Troy, NY. Active in the Society of Plastics Engineers since 1975, he currently serves on the boards of the Engineering Properties and Structures Division and Plastics Environmental Division of the SPE and was elected SPE Fellow in 2011. Dick is also a member of the American Chemical Society, American Physical Society and the Plastics Pioneers Association.

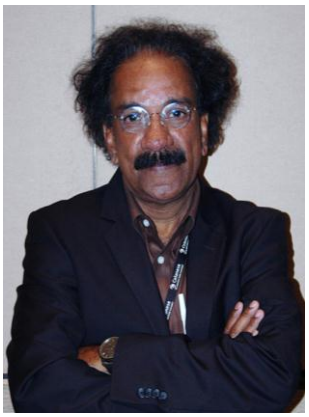
CONGRATULATIONS to Professor Shing-Chung (Josh) Wong!



Professor Josh Wong has been elected as a 2015 SPE Fellow with the nomination from our Engineering Properties & Structure Division. He will be inaugurated at SPE - ANTEC 2015.

Dr. Wong has made huge impacts in the following key areas:

- Pioneered the use of graphite platelet to improve electrical conductivity in PMMA. The key contributions that differentiate this work are its ability to improve the electrical conductivity at low concentrations using conventional melt compounding methods.
- Led the development of electro spun fibers and its application into dry adhesive formulation. This development has won support from NSF and Ohio State Board of Development to create a startup enterprise to scale up this technology commercially.
- Introduced the use of J-Integral fracture toughness developed for metals by Rice into large scale deformation in polymer fracture. This development has led to several key publications that later impacted subsequent research thoughts as it has been cited in many books and peer reviewed papers.



TPC Co-Chairpersons
Kaan Gunes, Oomann Thomas and Rishi Kumar (not pictured)

We are happy to report that EPSDIV will host 8 sessions in ANTEC 2015. Two of these sessions will be held jointly with the Composite Division. There will be 4 sessions held on Monday, and two each on Tuesday and Wednesday.

The session titles are:

- Structure Properties (3 sessions)
- Nanostructures, Properties, & Applications (2 sessions)
- Polymer Stability and Failure Analysis
- Material Processing, Fabrication, and Properties
- Polymer Morphology Characterization and Testing

A total of 43 papers are to be presented in these sessions. In addition to the oral presentations, EPSDIV will also host 4 poster sessions.

We have contacted and will have some of the most well-known names both in industry and academia to be keynote speakers, and it is our hope that this will add incentive to attract a bigger audience. In addition, strong and exciting sessions will help to promote EPSDIV and increase membership. The keynote and invited speakers who will provide industry overviews and technical highlights are:

Prof. Lawrence Drzal of Michigan State University, Prof. Behnam Pourdeyhimi of NC State, Prof. Sarah Morgan of University of Southern Mississippi, Prof. Alexander Chudnovsky of University of Illinois, Dr. Hsinjin Yang of Pioneer Scientific Solutions, Prof. Musa Kamal, Prof. Shaw Ling Hsu of U Mass, Amherst, Prof. Garth Wilkes of Virginia Tech, Prof. Tony Brennan of University of Florida, and Prof. Gilles Lubineau of KAUST.

Please note that three rooms have been reserved in the Orange County Convention Center in Orlando for the following EPSDIV meetings: Board Meeting on Sunday, March 22nd from 4-6 PM, the EPSDIV TPC meeting on Tuesday, March 24th from 11.30 AM to 1PM, and the EPSDIV Wine and Cheese Social on Tuesday, March 24th, 6PM-8PM.

Looking forward to seeing all of you at ANTEC 2015.

FINANCIAL REPORT
from July 1, 2013 to June 30, 2014

Emmett Crawford, Treasurer

Annual Financial Report for the Period:	**July 1, 2013 to June 30, 2014**	
Section/Division Name:	Engineering Properties and Structure Division	
Balance as of July 1, 2013	-1	**$ 30,659.24**
Cash, checking, savings, investments.		
*Equal to line **32** of prevous year's SPE Financial Report. On file with SPE HQ if needed*		

Income		**Actual**	**Budget**	**Variance**
Interest & Dividends	-2	$ -	$ 800.00	$ (800.00)
Monthly Meetings	-3	$ -	$ -	$ -
Board Meetings	-4	$ -	$ -	$ -
TOPCON Receipts	-5	$ -	$ -	$ -
Educational Programs	-6	$ -	$ -	$ -
Newsletter Ads / Sponsorships	-7	$ -	$ 6,000.00	$ (6,000.00)
Grant Contributions	-8	$ -	$ -	$ -
Scholarship Contributions	-9	$ -	$ -	$ -
SPE Rebate	-10	$ 7,450.62	$ -	$ 7,450.62
Award Sponsorship	-11		$ 1,000.00	$ (1,000.00)
ANTEC Sponsorship	-12	$ 4,490.10	$ 6,000.00	$ (1,509.90)
Misc. Inc	-13	$ -	$ -	$ -
Other: PMAD and Vinyl Division Joint Reception	-14	$ 4,350.00	$ -	$ 4,350.00
Other:	-15	$ -	$ -	$ -
Total Income (add lines 2 - 15)	-16	$ 16,290.72	$ 13,800.00	$ 2,490.72
Total Funds Available (add lines 1 and 16)	**-17**	**$ 46,949.96**	**$ 44,459.24**	**$ 33,149.96**

Expenses		**Actual**	**Budget**	**Variance**
General Office Expenses	-18	$ -	$ 100.00	$ (100.00)
Reception	-19	$ -	$ -	$ -
Board Meetings and Reception	-20	$ 7,594.19	$ 2,000.00	$ 5,594.19
TOPCON	-21	$ -	$ -	$ -
Educational Programs	-22	$ 500.00	$ -	$ 500.00
Newsletter Printing / Mailing	-23	$ 1,584.00	$ 1,000.00	$ 584.00
Awards	-24	$ 1,570.51	$ 2,000.00	$ (429.49)
Scholarships / Grants	-25	$ -	$ 1,000.00	$ (1,000.00)
ANTEC Expenses	-26	$ -	$ 1,000.00	$ (1,000.00)
Councilor Travel	-27	$ 1,322.23	$ 2,000.00	$ (677.77)
ANTEC TPC	-28	$ 485.00	$ 4,000.00	$ (3,515.00)
Teleconferences	-29	$ -	$ 1,000.00	$ (1,000.00)
BOD Travel	-30	$ -	$ 2,000.00	$ (2,000.00)
Bank Fees	-31	$ 80.04		
Total Expenses (add lines 18 – 30)	-32	$ 13,135.97	$ 16,100.00	$ (3,044.07)
Ending Balance (subtract line 31 from line 17)	**-33**	**$ 33,813.99**	**$ 28,359.24**	**$ 36,194.03**

SOCIETY OF PLASTICS ENGINEERS

REGISTER **ONLINE** TODAY!

www.antec.ws

Full Conference registration fee includes all Technical, Business & Plenary Sessions, NPE Show Floor, Networking Events, and access to the collection of Conference Proceedings.

ON-SITE REGISTRATION

Monday, March 23 - Tuesday, March 24
7:30 am - 5:00 pm

Wednesday, March 25
8:00 am - 2:00 pm

EXHIBIT HALL HOURS

Monday, March 23 - Thursday, March 26
9:00 am - 5:00 pm

Friday, March 27
9:00 am - 3:00 pm

HOTEL & TRANSPORTATION

A variety of hotels are available at different prices. Note that all hotel accommodations are handled for this event by the NPE Housing Team. Free shuttle bus service is available from **NPE2015** designated hotels and the Convention Center Monday through Friday (March 23-27) starting at 7:30 a.m. Routes and map are available through the link below. The local airport is Orlando International (MCO); for travel information, including air travel, car rental as well as airport shuttle, visit: **http://www.npe.org/general-information/travel-and-housing**

REFUND & CANCELLATION POLICY

Refunds will be granted through February 27, 2015 less a $100 processing fee. **No refunds granted after the February 27th deadline.** Registration may be transferred to an alternate person if requested. For cancellations or transfer of registration, contact SPE Customer Relations: +1 203.775.0471

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CONGRATULATIONS to Steven K. Burgess from Georgia Institute of Technology, selected as ANTEC 2014 Best Paper

DIFFUSION COEFFICIENT MODELING IN POLYESTER BARRIER MATERIALS: APPLICATIONS OF INFINITE SERIES SOLUTIONS

Steven K. Burgess‡, Robert M. Kriegel and William J. Koros‡*

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Abstract

While transport performance evaluation of new polyester resins can be accomplished through gravimetric or pressure-decay kinetic sorption experiments, estimation of model parameters can be challenging. Accurate diffusion coefficient determination is particularly difficult, as applications of the time-dependent diffusion equation yield non-intuitive infinite series solutions. Furthermore, complex diffusion processes often produce intractable models which require either short- or long-time approximations for parameter estimation. The current work circumvents such approximations by describing a modeling methodology useful for fitting complex infinite series solutions directly to experimental kinetic sorption data. Two specific modeling cases pertaining to polyester films are used to validate the methodology.

Introduction

Poly(ethylene terephthalate) (PET) has long been the industry standard for water and carbonated beverage containers [1]. Although PET has many desirable properties, an insufficient barrier to oxygen limits applications to more demanding markets such as fruit juice, beer, and vitamin water containers [2]. Evaluating the performance of more advanced resins to replace PET can be accomplished by estimating the permeability (P) through combination of the solubility (S) and diffusion (D) coefficients, i.e. $P = DS$ [3]. Kinetic sorption experiments are particularly useful for transport evaluation, as both D and S parameters can be determined through time-dependent penetrant uptake and equilibrium uptake, respectively. While accurate solubility coefficients are easily measured from the equilibrium penetrant uptake, modeling of the time-dependent approach to equilibrium can introduce large errors in the diffusion coefficient. Furthermore, significant errors arise when applying a simple Fickian model to diffusion cases where non-Fickian relaxations, non-constant boundary conditions, or combinations of the two factors are present.

The current work describes a MATLAB®-based modeling technique for extracting accurate diffusion coefficient information from complicated experimental kinetic sorption data, thus improving the accuracy of permeability predictions derived from this method. Kinetic sorption data has been collected via a pressure-decay method for non-condensable species such as oxygen and carbon dioxide. A simple normalization procedure allows a common framework for analysis by converting the raw data into the form of mass uptake at time t (M_t) divided by the mass uptake at infinite time (M_∞). Once normalized, the kinetic sorption curves can be modeled using known infinite series solutions of the time-dependent diffusion equation and relevant model parameters extracted through using a widely available non-linear least squares fitting routine. Since the infinite series solutions are discretized in MATLAB®, hundreds or thousands of terms in the infinite summation can be used easily to accurately approximate the model. Fickian models for non-constant and constant boundary conditions in films, cylinders, and spheres can also be incorporated into more complicated diffusion models which take into account non-Fickian relaxations, such as the Berens-Hopfenberg model.

The proposed method evaluates relevant model parameters after application of the discretized analytical model to the entire data set, and does not rely on short- or long-time analytical approximations as typically used in past methods [4]. The method therefore provides a more accurate estimation of the true diffusion coefficient which is uncomplicated by confounding long-term relaxations or sample geometry considerations. The ultimate result is a more realistic prediction of barrier properties through the relationship $P = DS$. The methodology is demonstrated and validated for two specific modeling cases involving diffusion in an infinite sheet: simple Fickian diffusion

with constant boundary conditions (O_2 in PET), and non-Fickian diffusion coupled with a variable boundary condition (CO_2 in poly(ethylene furanoate) (PEF)).

Materials and Experimental Methods

The poly(ethylene terephthalate) (PET) and poly(ethylene furanoate) (PEF) used in this study were provided by the Coca-Cola Company. PET exhibits an intrinsic viscosity (IV) of 0.84 dl/g, and the PEF is verified to have a high molecular weight. Carbon dioxide (CO_2) and oxygen (O_2) gases of 99.999% purity were provided by Airgas. Amorphous PET films were produced in a manner similar to Lee et al [5], and the amorphous morphology was verified through differential scanning calorimetry and x-ray diffraction.

Kinetic sorption data for O_2 and CO_2 were measured by a standard pressure-decay method [6] at 35°C. Since the pressure-decay method records pressure in the sample cell versus time, it is possible for highly sorbing penetrants to cause a significant drop in pressure from the start to end of the experiment. For such cases, the concentration of gas at the polymer surface will not be constant throughout the diffusion process and the variable pressure must be taken into consideration during diffusion modeling. Oxygen exhibits a low solubility in PET and therefore a constant boundary condition during the diffusion process is more valid. Alternatively, CO_2 exhibits a relatively high solubility in PEF and a variable boundary condition is needed to accurately model the diffusion process.

Diffusion Equations

The differential equation used to describe diffusive transport of a penetrant in a polymer is shown in Equation 1, which represents diffusion in an isotropic material and neglects convective transport and chemical reaction terms [7].

$$\frac{\partial C_i}{\partial t} = div\left(D\nabla C_i\right) \tag{1}$$

Where D is the diffusion coefficient (cm^2/s), C_i is the mass or molar concentration of species i, and div represents the divergence. Equation 1 simplifies to Equation 2 for diffusion in an infinite sheet and where D is constant. Analytical solution of Equation 2 requires one initial condition (usually $C = C_o$ at $t = 0$ for all x) and two boundary conditions (usually $C = C_1$ at $x = \pm L$ for all t, where L is the film half thickness) for simple Fickian diffusion.

$$\frac{\partial C_i}{\partial t} = D\frac{\partial^2 C_i}{\partial x^2} \tag{2}$$

The analytical solution of Equation 2 for the case of Fickian diffusion in PET (i.e. O_2 in PET) with constant boundary conditions is represented in Equation 3 [4] in the form of mass uptake at time t (M_t) divided by mass uptake at infinite time (M_∞), where L represents the film half-thickness. The only adjustable parameter in Equation 3 is the diffusion coefficient, which is effectively constant over the concentration interval of diffusion.

$$\left.\frac{M_t}{M_\infty}\right|_{Fick} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right) \tag{3}$$

Equation 3, which represents simple Fickian diffusion, can be modified to account for additional long-term relaxation effects through incorporation into the Berens-Hopfenberg (BH) expression shown in Equation 4. The BH model [8] considers first-order relaxations by assuming a linear superposition of relaxation and Fickian diffusion terms. In Equation 4, k (1/s) is the rate constant for the first-order relaxations and φ_F (-) is the weighting factor (ranging from 0-1) between Fickian and relaxation contributions.

$$\left.\frac{M_t}{M_\infty}\right|_{BH} = \left[\varphi_F\left(\left.\frac{M_t}{M_\infty}\right|_{Fick}\right) + (1-\varphi_F)\left(1-\exp(-kt)\right)\right] \tag{4}$$

Equations 3 and 4 accurately describe diffusion of O_2 and alcohols [9] in PET, respectively, but are not sufficient for modeling CO_2 diffusion in PEF. As mentioned previously, the high solubility of CO_2 in PEF can result in a significantly different pressure from start to end of the diffusion process. For such cases, solution of Equation 2 requires implementation of a variable boundary condition. The solution for this case is provided by Crank [4] and is reproduced in Equations 5-7.

$$\left.\frac{M_t}{M_\infty}\right|_{F,V} = 1 - \sum_{n=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^{\,2}}\exp\left(\frac{-Dq_n^{\,2}t}{L^2}\right) \tag{5}$$

$$\tan\left(q_n\right) = -\alpha q_n \tag{6}$$

$$\frac{n_{film,\,final}}{n_{total,\,initial}} = \left(\frac{1}{1+\alpha}\right) \tag{7}$$

Modeling of the variable boundary condition is captured in the α and q_n values in Equation 5, where α is defined in Equation 7 and is related to the final fractional uptake of the film after diffusion is complete. The q_n values are calculated from the non-repeating positive roots of the transcendental equation in Equation 6. Logically, Equation 5 simplifies to Equation 3 in the limit of $\alpha = \infty$.

While Equation 5 accounts for the variable pressure during a CO_2 sorption experiment, it fails to capture the long-term relaxations often induced by CO_2 conditioning. To account for these relaxations, the solution in Equation 5 can be combined with the Berens-Hopfenberg model to give a solution in the form of Equation 8 (referenced as BH-V from this point forward, where the "V" represents the Fickian solution after implementation of the variable boundary condition).

$$\left.\frac{M_t}{M_\infty}\right|_{BH-V} = \left[\varphi_F\left(\left.\frac{M_t}{M_\infty}\right|_{F,V}\right) + (1-\varphi_F)\left(1-\exp(-kt)\right)\right] \quad (8)$$

Equations 6-8 now provide an accurate description of the CO_2 diffusion process in PEF and should yield valid diffusion coefficients when modeled directly to experimental data. Although seemingly complex, all diffusion models presented thus far in Equations 3, 4, 5, and 8 can be easily implemented using the proposed modeling methodology.

Modeling Methodology

Before modeling the experimental kinetic sorption data, the data must be transformed into the form of M_t/M_∞ from the pressure-decay data and imported into MATLAB®. Equation 9 shows the transform for the pressure-decay data, where p is the sample pressure and *initial* and *final* represent the pressure measured at the beginning and end of the diffusion process, respectively.

$$\frac{M_t}{M_\infty}(t) = \left(\frac{p_{initial} - p(t)}{p_{initial} - p_{final}}\right) \quad (9)$$

In addition to transforming the pressure data, the time data (in seconds) must exist such that $t = 0$ represents the beginning of the diffusion process. Once transformed, the data is saved into an empty excel file (*currentData.xlsx*) such that the time data resides in the "A" column and the M_t/M_∞ data in the "B" column. Upon initializing MATLAB®, the "*xlsread*" command is used to import the kinetic sorption data. This command imports the data into MATLAB® such that the "*x*" matrix contains the time data and the "*y*" matrix contains the M_t/M_∞ data.

```
A = xlsread('currentData.xlsx');
x = A(:,1);
y = A(:,2);
```

The proposed modeling technique uses a widely available non-linear least squares fitting routine available on the MathWorks website [10]. This routine, entitled "*easyfit*," is useful because it applies any user-defined function to the entirety of the experimental dataset and provides the relevant model parameters based on the optimized fit. The command shown below is a simplified syntax for the *easyfit* routine, where *pbest* is the matrix containing the output model parameters (i.e. *D* for the Fickian model), *x* and *y* represent the experimental kinetic sorption data (which has already been imported into MATLAB® using the *xlsread* command), [*IG*] represents the matrix containing the initial guess of the model parameters, and *@function* represents the function name for the user-defined function.

```
[pbest]=easyfit(x,y,[IG],@function)
```

The remaining step is to define the function file that the routine will use to fit the desired model to the experimental data. Shown below is the function to implement the simple Fickian model with constant boundary conditions from Equation 3. The *U* matrix in the function syntax represents the matrix containing the adjustable model parameters (e.g. *D* is the only adjustable parameter for the simple Fickian case). In the function code, *U(1)* represents the first adjustable model parameter, or the diffusion coefficient. The dimension of the [*IG*] matrix and *U* matrix must be the same. For example, since there are three adjustable parameters in the BH model, the [*IG*] matrix will take the form of [*value, value, value*] and the adjustable parameters will take the form of *U(1)*, *U(2)*, and *U(3)* in the respective code. The benefit of using an entire function file to represent the model rests in the ability to discretize the infinite summation by using a "*for*" loop. Using this technique, the number of terms in the infinite series can be changed by altering the number of iterations in the loop.

```
function y=Fick(U,x)
L = 0.00226;            %Half-film thickness in cm
Sum = 0;
for i = 0:1:100;        %Number of terms in the infinite series
   m = 8/(pi^2*(2*i+1)^2)*exp(-U(1)*(2*i+1)^2*pi^2*…
   x./(4*L^2));
   Sum = m + Sum;
end
y = 1 - Sum;
end
```

The following syntax is used to apply the Fickian model directly to the experimental data:

```
[pbest]=easyfit(x,y,[1e-9],@Fick)
```

Once executed, the MATLAB® output is the [*pbest*] matrix and a graph of the optimized model plotted along with the experimental data. The [*pbest*] matrix contains the optimized values of the adjustable parameters from the selected model, i.e. [*pbest*] will contain one value for the simple Fickian fit and three values for the BH fit.

Extension of the function file to represent solutions of more complex diffusion problems is straightforward. For

CO_2 diffusion in PEF, application of Equation 8 requires solution of the transcendental equation in Equation 6. The non-repeating solutions of Equation 6 can be computed using MATLAB®'s *fzero* command, and the following code is useful for storing the first "*n*" positive solutions of Equation 6 into the vector q_n.

```
n = 100;
ep = 1e-4;
qn = zeros(1,n);
for i = 1:n
  qn(i) = fzero(@(q) tan(q)+alpha*(q),[pi/2+(i-1)*pi+ep
  pi/2+i*pi-ep]);
end
```

Calculation of q_n can be included in the larger function file specific to Equation 8. As a result, the function file for modeling CO_2 diffusion in PEF is shown below. The adjustable parameters for the BH-V model from Equation 8 are assigned as follows: *U(1)* = *D* (cm^2/s), *U(2)* = φ_F (-), and *U(3)* = *k* (1/s).

```
function y = BH_V(U,x)
L = 0.0107;              %Half-film thickness in cm
alpha = 2.0329;          %Obtained from Equation 7
n = 100;                 %Number of terms in the infinite series

ep = 1e-4;
qn = zeros(1,n)
for i = 1:n              %Calculating solutions of Equation 6
  qn(i) = fzero(@(q) tan(q)+alpha*(q),[pi/2+(i-1)*pi+ep
  pi/2+i*pi-ep]);
end

 Sum = 0;
for i = 0:1:n-1;
   m = 2*alpha*(1+alpha)/(1+alpha+alpha^2*qn(i+1)^2)*
   exp(-U(1)*(qn(i+1))^2*x./L^2);
   Sum = m + Sum;
end
w = 1 - Sum;
y = U(2)*w + (1 - U(2))*(1 - exp(-U(3)*x./1));  %BH model
end
```

Execution of the BH-V model is performed by the following command:

```
[pbest]=easyfit(x,y,[5e-10,1,5e-7],@BH_V)
```

The output from executing this command is again a graph of the model along with the experimental data and the [*pbest*] matrix, which now contains three optimized values. Care should be taken when selecting the initial values for the [*IG*] matrix. Since this procedure utilizes a non-linear least squares fitting routine, bad initial guesses can yield non-physical model results. Minor trial and error is recommended to verify the accuracy of the modeling results. As an example, a good initial value for the diffusion coefficient in the BH or BH-V model is the optimized value obtained after modeling the simple Fickian fit to the model data. A good initial value for φ_F is usually 1 or 0.5, based on the nature and magnitude of deviations from fits to Equation 3 [8], and a good initial value for *k* is ~1e-5 1/s. Clearly, optimized model outputs of φ_F which are negative or greater than one are non-physical and the initial guess parameters should be adjusted. In some cases, initial guesses of φ_F and *k* in the BH model can be obtained by the long-time approximation procedure outlined by Patton et al [11]. The MATLAB® files containing the previously described function definitions are also available upon request.

Results and Discussion

Fickian Diffusion, O_2 in PET

The simple Fickian model given in Equation 3 is valid for modeling O_2 sorption in PET. Figure 1 shows a graph of experimental O_2 sorption data in PET during the pressure step going from vacuum to 3.6 atm O_2. The film thickness used in the model represents an average thickness of ~45.2 ± 0.8 µm. The pressure-decay data is slightly noisy due to the low solubility of O_2 in PET (i.e. the pressure drop from the beginning to end of the diffusion process is only ~0.6 psia).

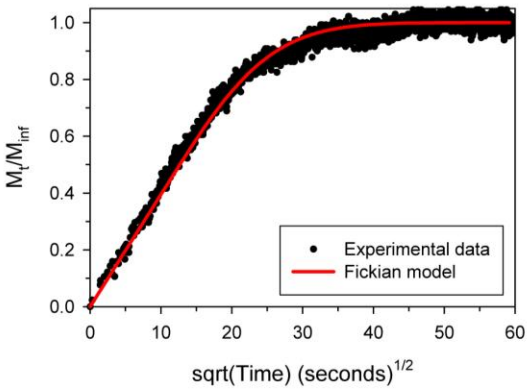

Figure 1. O_2 sorption in PET at 35°C. The Fickian model fit to the data is shown in red. The model represents 100 terms in the infinite series.

The diffusion coefficient for O_2 in PET at 35°C obtained from the Fickian model shown in Figure 1 is 6.3e-9 cm^2/s, and agrees well with other literature reports [12, 13].

Non-Fickian Diffusion, CO_2 in PEF

The Berens-Hopfenberg (BH) model coupled with a Fickian solution involving variable boundary conditions accurately models the kinetic transport of CO_2 in PEF. To

illustrate the utility of this modeling technique, it is useful to compare CO_2 diffusion coefficients obtained from all three modeling equations mentioned thus far against the same dataset. Figure 2 shows the Fickian model fit for experimental CO_2 sorption data in PEF during the pressure step from vacuum to 0.82 atm CO_2. The film thickness represents an average thickness of 214.6 ± 1 μm, and the high solubility of CO_2 in PEF yields a good signal-to-noise ratio in the pressure-decay data and a value of 2.03 for α. Figure 3 shows the experimental CO_2 sorption data along with the BH model fit from Equation 4, and Figure 4 shows the BH-V model fit from Equation 8. Relevant model parameters for all three models are given in Table 1, along with a comparison between predicted CO_2 permeability from $P=DS$ and actual experimental permeability results at 35°C.

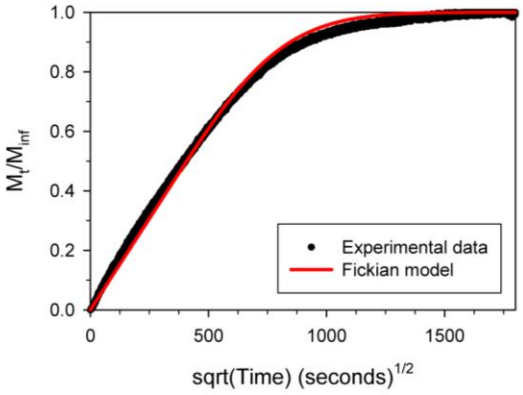

Figure 2. CO_2 sorption in PEF at 35°C. The Fickian model fit from Equation 3 is shown in red. The model represents 100 terms in the infinite series.

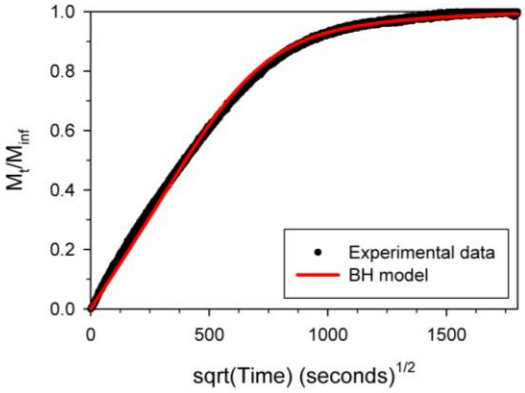

Figure 3. CO_2 sorption in PEF at 35°C. The Berens-Hopfenberg (BH) model fit from Equation 4 is shown in red. The model represents 100 terms in the infinite series.

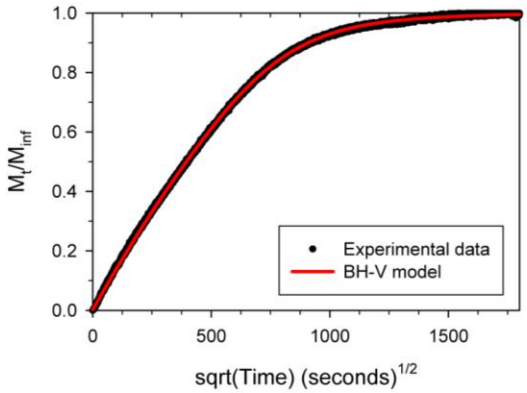

Figure 4. CO_2 sorption in PEF at 35°C. The red line represents the BH-V model fit from Equation 8. The model represents 100 terms in the infinite series.

Table 1. Relevant model parameters for CO_2 in PEF at 35°C.

	Fick	BH	BH-V
D (cm^2/s)	1.4e-10	1.7e-10	1.0e-10
φ_F (-)	—	0.87	0.91
k (1/s)	—	8.8e-7	8.9e-7
$\left(\frac{P_{P=DS} - P_{exp}}{P_{exp}}\right)100\%$	42	81	4.2

A comparison of Figures 2-4 reveals that the BH-V model provides the best fit to the experimental CO_2 kinetic sorption data. The applicability of the BH-V model is again seen in Table 1, where the permeability prediction through using the D from the BH-V model exhibits only 4.2% error while the Fickian and BH models exhibit 42% and 81% errors, respectively. The errors introduced in the permeability prediction through use of the incorrect diffusion model are therefore significant and can be avoided through use of the proposed modeling technique. As a note, the experimental permeability used in Table 1 (P_{exp}) was measured at 1 atm CO_2, and provides a meaningful comparison with the kinetic sorption data recorded at ~0.82 atm CO_2.

Extensions to More Complex Geometries

Although the proposed modeling technique has only been illustrated for two specific diffusion cases in an infinite sheet, the methods are applicable to more complex geometries and to analogous heat conduction problems. The only requirement is that the analytical solution of the differential equation be known and that all experimental parameters needed by the model are accurately characterized (accurate sample dimensions, etc). Tabulations of diffusion equation solutions are provided

by Crank [4], while analytical solutions of the heat conduction equation are provided by Carslaw and Jaeger [14].

Conclusions

Accurate determination of transport parameters, including the solubility and diffusion coefficients, is important for estimating penetrant permeability from kinetic sorption data. The current methodology provides a framework for applying known diffusion models to experimental kinetic sorption data, with special applicability to complex diffusion models. While demonstrated for only two specific diffusion cases, the proposed methodology is applicable to a wide range of diffusion and heat conduction problems.

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Keywords

Diffusion coefficient, modeling, non-Fickian, relaxations