

News



The Society of Plastics Engineers

ENGINEERING PROPERTIES
& STRUCTURE DIVISION

December 2012

Chairperson's Report



Dear EPSDIV Members,

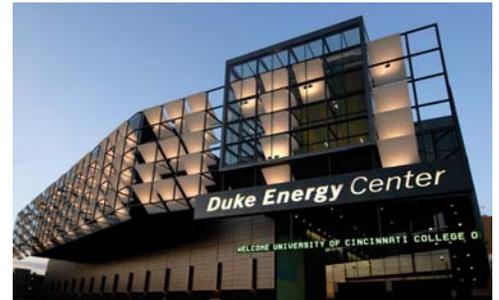
It is once again approaching the year end as we all celebrate the holiday seasons. We also celebrated a year of professional accomplishments. SPE provides a venue for us to interact with each other professionally, establish and rejuvenate business and technical networks, and nurture the next generation plastics engineers domestically and across the globe. SPE has been increasingly crossing borders and venturing out into other developed and emerging markets, building relationships with local plastics industries. We are proud to be among one of the most active divisions in SPE. As I write this letter, three of our senior members of the EPSDIV Board, Steve Driscoll, Brian Grady, and Sadhan Jana, are participating in ANTEC Mumbai 2012 in India. EPSDIV is also supporting SPE's

Opportunities Abound!

efforts in EuroTech 2013 and are planning to organize a Topcon in the 2013 SPE China Conference with Daniel Liu, John Trent and myself planning to participate. Additional board members are likely to join us at a later date. Milan Ivosevic and Theresa Hermel-Davidock, our Technical Program co-Chairs, are actively organizing the EPSDIV ANTEC 2013 sessions at the Duke Energy Convention Center in Cincinnati, OH. Also, our Division continues to support student participation in the John O'Toole Award and the International Award. We have a sound balance sheet, thanks to the work done by every board member, including our treasurer, Emmet Crawford. John Trent, our Chair-Elect and newsletter editor, is actively preparing the Division's Pinnacle Award application, which is due at year end. We look forward to an exciting year coming up with a host of opportunities to develop our professional connections and new businesses, through SPE.

Before my next communication, I wish you all a Merry Christmas and a Happy New Year!

Shing-Chung "Josh" Wong



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Milan Ivosevic and Theresa Hermel-Davidock



Symposium in honor of Prof. Avraam Isayev

The symposium has been organized by Prof. Sadhan C. Jana including the following invited speakers:

- **Prof. Musa Kamal**, McGill University
- **Prof. Petr Saha**, Thomas Bata University, Zlin, Czech Republic
- **Prof. Miko Cakmak**, University of Akron
- **Prof. Eric Baer**, Case Western Reserve University
- **Prof. David Kazmer**, UMass Lowell
- **Prof. Mahesh Gupta**, Michigan Tech

In preparation for the ANTEC 2013 in Cincinnati, TPC's have finalized arrangements for the upcoming paper review activities and session allocations. A total of 24 EPSDIV members have accepted to serve as conference paper reviewers to date. An extra effort has been made to ensure that the reviewers receive the papers that are closely related to their expertise in order to facilitate a high quality review process.

The following invited speakers have already confirmed their ANTEC 2013 participation ensuring that some of the EPSDIV core focus areas are covered by the keynote talks. Additional speakers have been identified and will be invited after defining and structuring sessions following the paper review process.

- **Prof. Melissa Grunlan**, Texas A&M University
- **Prof. Jaime Grunlan**, Texas A&M University
- **Kim Walton, PhD**, The Dow Chemical Company
- **Prof. Cris Schwartz**, Iowa State University
- **Jorgen Bergstrom, Ph.D.**, Veryst Engineering

New Technology Forum "Polymer Applications in Health"

This forum has been scheduled for Wed. (4/24) afternoon during the ANTEC 2013 and is jointly hosted by Engineering Properties and Structures Division and Medical Plastics Division.

Co-Chairs are:

- **Prof. Sadhan C. Jana**, University of Akron
- **Len Czuba**, President of Czuba Enterprises, Inc.

Two Best Paper Award Winners were selected at ANTEC 2012

Congratulations to:

- **Daniel Schmidt, et. al.**, Mechanical Properties of Cycloaliphatic Terephthalate Co-polyester Clay Nanocomposites
- **Luyi Sun, et. al.**, Preparation of Intercalated Organic/Inorganic Hybrids via In-Situ Synthesis

These papers are presented at the end of this newsletter starting on page 9

Financial Report from July 1, 2011 to June 30, 2012



SPE ANNUAL FINANCIAL REPORT

Annual Financial Report for the Period: July 1, 2011 to June 30, 2012
Section/Division Name: Engineering Properties and Structure Division

Balance as of July 1, 2011 -1 \$ **37,944.56**

Cash, checking, savings, investments.

Equal to line 32 of previous year's SPE Financial Report. On file with SPE HQ if needed

Income		Actual	Budget	Variance
Interest & Dividends	-2	\$ 505.71	\$ 800.00	\$ (294.29)
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	\$ 2,747.66	\$ -	\$ 2,747.66
Award Sponsorship	-11	\$ -	\$ 1,000.00	\$ (1,000.00)
ANTEC Sponsorship	-12	\$ 6,631.10	\$ 6,000.00	\$ 631.10
Misc. Inc	-13	\$ -	\$ -	\$ -
Other:	-14	\$ -	\$ -	\$ -
Other:	-15	\$ -	\$ -	\$ -
Total Income (add lines 2 - 15)	-16	\$ 9,884.47	\$ 13,800.00	\$ (3,915.53)
Total Funds Available (add lines 1 and 16)	-17	\$ 47,829.03	\$ 51,744.56	\$ 34,029.03

Expenses		Actual	Budget	Variance
General Office Expenses	-18	\$ -	\$ 100.00	\$ (100.00)
Reception	-19	\$ -	\$ -	\$ -
Board Meetings and Reception	-20	\$ 1,899.58	\$ 2,000.00	\$ (100.42)
TOPCON	-21	\$ -	\$ -	\$ -
Educational Programs	-22	\$ -	\$ -	\$ -
Newsletter Printing / Mailing	-23	\$ 1,584.00	\$ 1,000.00	\$ 584.00
Awards	-24	\$ 2,500.00	\$ 2,000.00	\$ 500.00
Scholarships / Grants	-25	\$ -	\$ 1,000.00	\$ (1,000.00)
ANTEC Expenses	-26	\$ 808.34	\$ 1,000.00	\$ (191.66)
Councilor Travel	-27	\$ 3,539.76	\$ 2,000.00	\$ 1,539.76
ANTEC TPC	-28	\$ 3,500.00	\$ 4,000.00	\$ (500.00)
Teleconferences	-29	\$ -	\$ 1,000.00	\$ (1,000.00)
BOD Travel	-30	\$ -	\$ 2,000.00	\$ (2,000.00)
Bank Fees	-31	\$ 33.00	\$ -	\$ 33.00
Total Expenses (add lines 18 - 30)	-32	\$ 13,864.68	\$ 16,100.00	\$ (2,268.32)
Ending Balance (subtract line 31 from line 17)	-33	\$ 33,964.35	\$ 35,644.56	\$ 36,297.35

Allocation of Funds on Line 32 (enter allocations as applicable)			
Checking Account		(A)	\$ 33,964.35
Savings Account 1		(B)	\$ -
Savings Account 2		(C)	\$ -
Investment 1		(D)	\$ -
Investment 2		(E)	\$ -
Investment 3		(F)	\$ -
TOTAL		(G)	\$ 33,964.35

Amount on line G should equal amount reported on line 32

Section / Division Treasurer's Name: Emmett Crawford

Engineering Properties and Structure Division

BALLOT

Board of Directors Nominees

(Please Vote for Six of the Following Six Candidates)

EMAIL your choices for Board members by **January 31, 2013**
to Dr. John S. Trent at jstrent@scj.com

Dr. Brian Grady

Brian Grady received a B.S. from the University of Illinois in 1987, and a PhD from the University of Wisconsin in 1994, both in Chemical Engineering. Since 1994, he has been employed by the University of Oklahoma as a faculty member in the School of Chemical, Biological and Materials Engineering and currently is the Conoco-DuPont Professor of Chemical Engineering. He has authored over 100 refereed publications and book chapters and is also the author of a new book entitled “Carbon Nanotube-Polymer Composites Manufacture, Properties and Applications” published by Wiley. He has served on the EPSDIV board since 2003, and served as chair of the Division for 2007-2008. He also served on the Executive Committee of the Society of Plastics Engineers from 2008-2012 and served as Secretary of the Society in 2010-2011. He was elected as a Fellow of the Society in 2012.

Dr. Kaan Gunes

Dr. Kaan Gunes is a native of Istanbul, Turkey. He received his B.S. in Chemical Engineering at Bogazici University in 2004. He then went on to pursue a Ph.D. in Polymer Engineering at the University of Akron under the supervision of Prof. Avraam Isayev. His Ph.D. dissertation was entitled “In-situ Ultrasonic Compatibilization of Binary Blends of Flexible Chain Polyesters and Aromatic Liquid Crystalline Polymers.” Following the completion of his Ph.D. in 2009, Dr. Gunes returned to Turkey to join Kordsa Global of Sabanci Corporation, which produces industrial textiles and tire cord, as a Project Leader in the New Product and Process Development Platform. Dr. Gunes earned Six Sigma Black Belt and Project Management Professional (PMP) certifications in 2011. In the same year, Dr. Gunes was also awarded the Sabanci Corporation Golden Collar Innovation Award. Since October 2011, Dr. Gunes has been working as an Advanced Polymer Applications Engineer at the Eastman Chemical Company, based in Kingsport, TN. Dr. Gunes currently supports the development and specification of Eastman copolyesters for a wide range of molding applications. Dr. Gunes has been an SPE member since 2004. He has served on the SPE Akron Section Board of Directors and the Education board from 2005-2009. He also served as the president of the SPE Akron Section Student Chapter at the University of Akron from 2005-2006. During his presidency, Dr. Gunes led the Student Chapter into winning both the SPE Stretch Outstanding Student Chapter, and SPE Chase Education Awards, for which he was awarded the Most Outstanding Leader honor by The University of Akron in 2006. Dr. Gunes served as co-organizer, moderator, and scientific advisor in the Polymer Processing Society 2010 conference in Istanbul, Turkey. He was also a co-organizer in the SPE Thermoplastic Elastomers 2007, and Polymer Display Technologies 2006 conferences in Akron, OH. Dr. Gunes has co-authored 13 peer reviewed publications, and delivered close to 20 presentations in national and international conferences, including four at SPE ANTEC.

Dr. Mridula (Babli) Kapur

Mridula (Babli) Kapur is a Principal Research Scientist in the Dow Chemical Polyethylene and Packaging business. She joined Dow in 1991, in Tarragona, Spain, after obtaining her PhD in Chemistry from Texas A&M University. She relocated to Dow Texas Operations in 1998. Her primary area of expertise is in flexible and rigid packaging product development. She has 4 granted patents, 13 pending priority applications and several external publications. Babli served on the SPE Blow Molding Division board of directors from 2009-12.

Engineering Properties and Structure Division

BALLOT (Cont.)

□ Dr. Daniel Liu

Dr. Daniel Liu is currently a Senior Associate in the Polymer Science & Materials Chemistry Practice at Exponent, Inc., an engineering and scientific consulting firm. His expertise includes polymer, composite and nanocomposite technologies, polymer toughening and strengthening, fracture mechanisms, structure-property relationships, material evaluation and failure analysis. He also has specific experience with root cause analysis for failures of coatings and adhesives, plastic pipes, fuel containers, plastic wheels/rims, medical devices and consumer electronics, among other polymeric products or components. Prior to joining Exponent, he conducted research in development and performance of toughened epoxies, polyolefins, nanocomposites, biodegradable polymers, food packaging and electronic packaging materials. He has authored 2 book chapters and more than 40 peer-reviewed journal papers or conference technical papers. Dr. Liu earned his B.S. in Polymer Materials and Engineering from Fudan University, China, his M.Phil. in Mechanical Engineering from Hong Kong University of Science and Technology, and his Ph.D. in Materials Science and Engineering from Texas A&M University. Dr. Liu is currently a Senior Member of SPE and a Board Member of Engineering Properties and Structures Division (EPSDIV). He also serves as the Chair of the Awards Committee at EPSDIV and is responsible for selecting the Best Paper Award and John O'Toole Award for each year's ANTEC meeting.

□ Dr. Daniel F. Schmidt

Dr. Schmidt graduated with University Honors from Carnegie Mellon University (1998) with a B.S. in Materials Science & Engineering and a B.S. in Chemistry. His Ph.D. in Materials Science & Engineering was earned at Cornell University (2003) under the direction of Prof. Emmanuel P. Giannelis on the subject of silicone nanocomposites. He served as a post-doc in the newly formed BASF group in Nobel Laureate Jean-Marie Lehn's Institut de Science et d'Ingénierie Supramoléculaires (ISIS) in Strasbourg France, where he developed methods for the production of nanoporous materials currently being scaled up under the tradename ISITECT®. He joined the Department of Plastics Engineering at the University of Massachusetts Lowell in 2005, where his work concerns polymer nanocomposites, sol-gel derived networks (responsive hydrogels, tissue engineering scaffolds), pre-ceramic polymers and sustainable materials (plant-derived plasticizers and alternative epoxy resins). In 2009 he was honored as the first recipient of the Mark and Elisia Saab Endowed Professorship in Sustainable Plastics Engineering, and in 2011 he was granted tenure and promoted to Associate Professor. He has served as a member of the Board of Directors of the Engineering Properties and Structure Division (EPSDIV) of the Society of Plastics Engineers since 2010, and in this capacity he is currently a member of the internet subcommittee.

□ Dr. Luyi Sun

Luyi Sun is an assistant professor of chemistry at Texas State University–San Marcos. Professor Sun received his B.S. in Polymer Chemical Engineering from South China University of Technology (Guangzhou, China) in 1998 and his Ph.D. in chemistry. Early 2005, Dr. Sun joined Polymer Technology Center at Texas A&M University (TAMU) as an assistant research engineer. His research at TAMU focused on the synthesis of nanomaterials and preparation of nano-structured composites for structural, functional, and energy related applications. Dr. Sun joined Total Petrochemicals USA, Inc. (La Porte, TX) in 2006 to develop new polyolefin based materials for various applications. During his three year-stint in Total, Dr. Sun led a team and developed several key technologies on polypropylene blow molding, biodegradable polymer packaging materials, and high performance nanocomposites that led to 17 US/International patents/patent applications. In 2009, Dr. Sun joined the Department of Chemistry and Biochemistry and Materials Science, Engineering, and Commercialization Program at Texas State University–San Marcos as an assistant professor. His research focuses on materials science, with a focus on using chemistry as a key tool to design new materials. Dr. Sun has authored over 50 scientific papers in peer-reviewed journals, two book chapters, and delivered over 60 talks at national/international conferences. He is also the inventor or co-inventor of 29 US/International Patents/Patent Applications. Dr. Sun served as the technical program chair for EPSDiv at ANTEC 2011, set up the SPE Student Chapter at Texas State University–San Marcos in 2009 and has served as the faculty adviser for the student chapter since then.

A Message to All SPE Student Chapter Advisors ***The John O'Toole Outstanding Undergraduate*** ***ANTEC Paper Award***

Since the 1980s EPSDIV has sponsored the John O'Toole Memorial Award for Outstanding Undergraduate Student Paper presented at ANTEC. This globally-recognized award, which includes a one-thousand dollar stipend and recognition plaque, is generously funded by The Honeywell Corporation in memory of its outstanding Allied Chemical employee, John O'Toole.

Through the years this award has been presented to undergraduates (or team of undergraduates) who have delivered podium presentations on a myriad of topics, including alloys & blends, thermoplastic composites, innovative packaging materials and modified elastomers.

EPSDIV invites undergraduates to submit papers for presentation at ANTEC 2013 in Cincinnati, Ohio. A committee of EPSDIV members will review these papers and the finalists will be incorporated into the EPSDIV-sponsored ANTEC podium presentation schedule. Each finalist will also be offered an EPSDIV-sponsored SPE Student membership.

To be considered for the O'Toole Award, undergraduates students should simply follow the ANTEC paper submission requirements and observe the deadlines for all ANTEC papers. Additionally, at the same time, a separate copy of your paper should be mailed directly to Dr. Daniel Liu* for EPSDIV panel review. The author(s)' undergraduate advisor's contact information must be included.

If you have any questions, please email Dr. Daniel Liu: djliu@exponent.com

Mail papers to:

Dr. Daniel Liu
Exponent, Inc.
17000 Science Drive, Suite 200
Bowie, MD 20715

We look forward to your students participating in our EPSDIV awards competition.

Steve Driscoll
Secretary, EPSDIV

Encourage Others to Join EPSDIV,
By visiting: www.4spe.org/membership



A cliff, a precipice...would you walk up to the edge? That would terrify me. Instead I might opt to find a stream and just “drift”... a seemingly easy course that has its own direction. That would relax me. I’ve come to realize though, that drifting for extended periods of time can leave me in a far more precarious place than the proverbial cliff. The same may be true for science, our industry, and our careers.

The “cliff” is really a forced decision point. We are faced with predicting what would happen if we decide to stay where we are, or jump off. Our ensuing action plan, no matter which choice we make, involves the next steps forward. The fiscal cliff is a case in point. If we decide not to jump, it is because we have agreed to a newly determined landscape of future taxation, government spending, and debt. We have prioritized and will implement changes in each of these areas. However, if we decide to jump, then we have set in motion the plan to move forward with a specific pre-determined landscape. In either case we are moving forward. The question

Fiscal Cliff or Fiscal Drift!

will be – do we like where we are going?

The “drift” forced nothing. We go where we go. Enjoying the journey, but not really thinking about the destination. We may eventually find ourselves in a position where we have to formulate a plan of how to “get back” to somewhere we have already been. Time and resources are wasted backtracking in order to get where we could go in a different, specified direction. Drifting, although calm and relaxing, may deliver us to a far more frightening place than the cliff. We may not like where we are – and have no reasonable way to either get back or continue.

I think that all of this can ring true in science, in SPE, and in our careers as well. The “cliff” has forced prioritization in spending. It could trigger sweeping cuts to agencies across the federal government, including agencies like the National Science Foundation, National Institutes of Health, and others that provide the vast majority of the nation’s research and development funding. Research universities all depend on those funds to support faculty, staff, post doctoral studies, and graduate students, as well as to provide for equipment and facilities. Industry relies on this national scientific pipeline, and on the certainty that a specific, prioritized plan for moving forward is in place.

Drifting only postpones decisions, prioritization, and action. Without a plan for funding allocations or

cuts, some government agencies are holding back funding. That’s led to a near standstill in funding research grants, according to scientists and scientific lobbying groups. If the stagnation (drifting) were to continue, the real trouble would lie in long-term national scientific achievement. Lower grant acceptance rate means scientists have to devote more of their time to grant writing instead of focusing on actually planning and performing experiments. We start doing less science – as more of our time is going to preserving funding, thereby slowing scientific progress.

As we close out 2012 the “cliff” has become more attractive to me. We face one every year within our organizations, as we lay out specific plans for both our personal and organizational goals. We plan on a destination, and map out a route to get there. Within SPE we develop annual specific goals and plans to better serve our membership, and our industries. The same is true within the national scientific community. I know that all of you are involved in developing your own sets of professional goals. Don’t spend 2013 drifting. We need your voice, your expertise, and your energy to help us do the same within SPE. Finally, we need your insight and influence to help shape our national priorities. Are you looking for ways to be more involved in 2013? Contact me!

- *Brian Landes*

EPSDIV Board of Directors 2012-2013

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MECHANICAL PROPERTIES OF CYCLOALIPHATIC TEREPHTHALATE CO-POLYESTER CLAY NANOCOMPOSITES

Humza Jafferji¹, Daniel F. Schmidt¹ and Emmanuel Reynaud²

¹Department of Plastics Engineering

²Department of Mechanical Engineering

University of Massachusetts Lowell, Lowell, MA

Abstract

Polymer nanocomposites have been studied extensively and can provide many benefits, including enhanced mechanical, barrier and fire properties. This paper studies the effect of montmorillonite nanoclay in a primarily amorphous cycloaliphatic terephthalate co-polyester system. The measured tensile properties show increased stiffness coupled with retention of ductility (elongation at break) at low nanoclay loadings, contrary to expected trends. The morphology of these materials was analyzed in an attempt to understand the unusual effects of the nanoclay in this case.

Introduction

Polymer nanocomposites have become a popular material choice for many applications. Of the types of nanoparticles in common use, layered silicates are especially popular. The automotive and food packaging industries have both embraced these materials^[1] because of their ability to offer a unique set of properties, and they have found their way into commercial medical devices as well^[2].

Many studies have shown how material properties trend when layered silicates are added to a polymer matrix. The majority show enhancements in modulus, strength, heat resistance, chemical resistance, flame retardance and improved barrier properties when compared to the unfilled material^{[1][3]}. While conventional fillers can provide some of these enhancements as well, nanocomposites are unique in their promise to produce such properties at low nanofiller loading levels without substantially compromising other polymer features such as optical clarity^[4]. However, properties of the polymer nanocomposite are affected by how the layered silicate is incorporated into the polymer. Polymer/layered silicate nanocomposite systems may be intercalated, where polymer chains have penetrated in between silicate layers (clay galleries) but the layered silicates remain parallel and ordered. They can also form exfoliated systems, where the layers are individually separated and surrounded by polymer chains. The orientation of the layered silicates and the polymer chains strongly affects mechanical properties as well^[5]. Fundamentally, the polymer/layered silicate interaction also affects polymer

microstructure as well, with additional consequences for polymers properties.

In addition to their ability to alter polymer microstructure, nanoparticles are capable of unique interactions with polymer chains at the molecular level because their sizes are of the same order of magnitude. Some researchers have found that polymer chains under confinement (for example: one polymer chain in a pore or between silicate layers) change their thermal relaxation behavior (T_g)^[6] which can have an effect on mechanical/thermal properties.

In this study, a polymer nanocomposite was created using a saturated cyclic co-polyester and montmorillonite clay as the layered silicate. Montmorillonite clay is readily available and inexpensive in comparison to most other nanofillers. It is often used in polymer nanocomposites because of its regular, platy shape and high aspect ratio^[4]. The co-polyester used is commercially known as Tritan and is produced by Eastman Chemical Company. According to the manufacturer, this co-polymer exhibits excellent chemical resistance, toughness, optical properties, and high temperature resistance. The molecular structure for the co-polyester repeat unit is shown in Figure 1. The potential monomers used in the polymer synthesis are dimethyl terephthalate, 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO), and 1,4-cyclohexanedimethanol^[7].

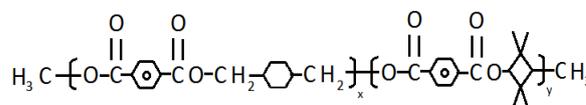


Figure 1. Molecular structure for co-polyester repeat unit studied in this paper.

This polymer nanocomposite system was chosen because of previous research on a similar system which showed novel mechanical behavior in the form of "simultaneous increases in stiffness and elongation at break."^[8]

Tensile tests were performed to assess changes in mechanical properties as a function of nanoclay addition. X-ray diffraction (XRD) and differential scanning calorimetry (DSC) were used to assess the thermal properties and microstructure of these materials.

Materials and Processing

Materials

The resin used is a co-polyester, developed by Eastman Chemical Company, poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol-co-cyclohexylene-dimethylene-terephthalate) (Trade name: Tritan, Grade: TX1000). The nanoclay used is Southern Clay Products' Cloisite 20A, a natural montmorillonite clay whose layer surfaces have been modified with dimethyl ditallow ammonium cations to render them compatible with less polar polymers. Mineral oil (STE Oil Crystal Plus Oil 70FG) was used as a processing aid in selected compositions.

Compounding

Nanocomposites were made using a 27 mm Leistritz co-rotating twin screw compounder with a 40:1 L/D ratio (Model ZSE-27HP-40D, Serial 60-04-03-08). A single gravimetric feeder was used (Brabender Technologie Model MDS-SW-10/SPlus-50). The pellets and nanoclay were dried at 88°C for 4 hours in a VWR Scientific forced air oven (Model 1350 FM). They were then vigorously shaken in a plastic bag to evenly distribute the nanoclay over the surface of the pellets. This pre-mix was placed into the feeder which fed into the primary feed port of the extruder. The resulting strand was pelletized (using a Reduction Engineering pelletizer Model 604) for further use in injection molding. Mineral oil was used during the pre-mixing process to enhance nanoclay adhesion to the exterior of the polymer pellets and create higher nanoclay loading level, thus suppressing settling in the feeder and dispersal in the air. The quantity of mineral oil used was driven by the oil's ability to coat the pellets, and typically amounted to ~20 g per batch of material (3-5 kg), or approximately 0.5 wt%. Nanofiller-free control samples with and without mineral oil were created to determine whether or not the mineral oil has an effect on the properties of the compound. The compositions created are named PNC (XX), where PNC stands for polymer nanocomposite and the number enclosed in parenthesis is the inorganic loading level in vol% or indicates a control group.

Injection Molding

An Arburg All-rounder Golden Edition 320 C injection molding machine was used. ASTM D638 Type IV tensile specimens were molded for each composition studied. The relevant temperature profile and other process settings are given in Table 1.

Table 1. Injection molding parameters

Parameter	Value
Feed Throat (°C)	23
Zone 1 (°C)	275
Zone 2 (°C)	275
Zone 3 (°C)	275
Zone 4 (°C)	275
Zone 5 (°C)	275
Mold Temperature (°C)	49
Screw Speed (m/min)	3
Shot Size (cm ³)	17.5
Injection Pressures (bar)	900-1200
Cooling Time (s)	20

Tensile Testing

Tensile testing was performed using an Instron load frame (Model 6025). Test specimens were conditioned for one week at 21°C and 50% RH. Instron Bluehill software (Version 2.6.440) was used to collect data and calculate selected mechanical properties. A modified ASTM D638 procedure was followed. Extension was determined via jaw separation. The test rate was 50 mm/minute. At least five specimens were tested per compound.

Thermogravimetric Analysis (TGA)

TGA was performed using a TA instruments Q50 TGA unit. The parameters used are shown in Table 2. Three pellets obtained at different times during the extrusion process were analyzed separately for each composition studied.

Table 2. TGA parameters.

Parameter	Value
Pan type	Platinum
Sample gas	Air
Sample as flow rate	60 mL/min
Temperature ramp rate	20°C/min
End Temperature	850°C

X-Ray Diffraction (XRD)

Analyses were performed using a Scintag XDS-2000 theta-theta powder diffractometer with a Cu K_α x-ray source ($\lambda = 1.54 \text{ \AA}$, using 1 and 2 mm divergence and scatter slits) and a liquid nitrogen cooled solid-state Ge detector (using 0.5 and 0.2 mm scatter and receiving slits). Samples consisted of ~30 mm long segments taken from the center of tensile bars and oriented with the injection direction perpendicular to the beam, with a 30 mm square single crystal quartz plate below each sample to ensure no background signal. Scans were performed over a range of 1-40° two-theta at a scan rate of 2.00°/minute with the x-ray tube energized at 45 kV and 40 mA to generate diffraction patterns.

Differential Scanning Calorimetry (DSC)

DSC was performed using a TA Instruments Q200 DSC unit. A heat/cool/heat procedure was used to erase the process history of the sample and to ensure good contact with the sample pan. The DSC parameters used are shown in Table 3. DSC samples were always taken from the center of injection molded tensile specimens.

Table 3. DSC parameters.

Parameter	Value
Pan Type	Tzero Aluminum Hermetic
Sample gas	Nitrogen
Sample gas flow rate	25 mL/min
Cycle 1	Ramp 10°C/min to 290°C
Cycle 2	Ramp 20°C to 40°C
Cycle 3	Ramp 10°C/min to 290°C

Results and Discussion

A summary of the TGA results is shown in Table 4. The compositions are differentiated by the inorganic content of the system due to the presence of the nanoclay. A range of compositions was created in order to assess nanocomposite behavior and properties as a function of nanoclay content. In addition to providing precise composition data, these results confirm the utility of mineral oil in reducing variability in inorganic content at the highest nanoclay loadings.

Table 4. Average inorganic content by volume

Composition	Inorganic Content (vol%)	Mineral Oil Present (Y/N)
PNC (no oil)	0 ± 0	N
PNC (oil)	0 ± 0	Y
PNC (0.15)	0.15 ± 0.01	N
PNC (0.26)	0.26 ± 0.03	N
PNC (0.5)	0.5 ± 0.1	N
PNC (0.73)	0.73 ± 0.03	Y
PNC (0.79)	0.79 ± 0.04	Y

The tensile properties of Tritan and its nanocomposites were studied, with the trends reported in Figures 2-6.

Figure 2 shows the average tensile modulus versus the inorganic content of the compositions. The modulus increases as the percent inorganic content increases, confirming the stiffening effect of the nanofiller. There is no statistical difference in the modulus between the control samples with and without oil, which means that the increase is due mainly to the addition of the nanoclay. Even at small concentrations the nanoclay is acting to reinforce the polymer.

Tensile stress and elongation at yield are shown in Figure 3 and Figure 4, respectively. Linear trends are

observed in both plots, with the addition of nanoclay resulting in an increase in tensile stress at yield coupled with a decrease in tensile strain at yield. As with tensile modulus, the mineral oil appears to have no effect on the yield behavior.

Analogous to the yield point figures, tensile stress and elongation at break are shown in Figure 5 and Figure 6, respectively. In this case an increase in both tensile stress and tensile elongation at break is observed up to 0.26 vol% inorganic content. At 0.5 vol% inorganic and above, however, a significant reduction in both values is observed, to tensile strength values on par with the base resin and elongation at break values below that of the base resin. The addition of more nanoclay makes little difference at this point, and in this composition range strain hardening is almost entirely suppressed. These observations imply fundamental changes in deformation and failure mechanisms. In support of this conclusion, an examination of PNC (no oil), PNC (oil), PNC (0.15), and PNC (0.26) tensile specimens shows relatively smooth and clean fracture surfaces. In contrast, compositions containing higher levels of nanoclay show rough, uneven fracture surfaces as well as skin formation.

This behavior goes against many of the observations of how amorphous polymers are expected to behave in the presence of nanoclay. In particular, this data suggests optimum nanoclay loadings may alter the polymer microstructure in unexpected ways, with clear consequences for failure mechanism and conditions.

The physical appearance of the tested specimens was also observed to change during testing. The co-polyester material as received is clear with no haziness. The specimens created using the PNC (oil) composition which contains colorless food grade mineral oil did display slight haziness but remained transparent. As the loading levels increased the specimens gradually acquired a yellow/brown tinge. The specimens created using PNC (0.73) and PNC (0.79) compounds also had a slightly hazy look as a consequence of the addition of mineral oil. However, all of the specimens remained transparent in the unstressed state. During tensile testing, however, whitening was observed specifically in those specimens containing nanoclay, with nanoclay-free samples retaining their transparency throughout. This provides further evidence that the nanoclay is affecting polymer microstructure and deformation mechanisms in the polymer nanocomposites.

DSC was used to determine the effect of nanoclay on the morphology and thermal transitions of the co-polyester. The glass transition temperature (T_g), crystallization temperature (T_c), and melt temperature (T_m) are important thermal transitions which can be determined from DSC data. The percent crystallinity was determined using the heat of fusion of PET^[9], based on a recommendation from the manufacturer and in the absence of specific data for the co-polyester studied here.

Table 5 summarizes the thermal transition data by composition.

By comparing PNC (no oil) and PNC (oil) compositions, it becomes evident that the mineral oil is acting to increase the ability for the material to crystallize. In particular, the mineral oil appears to be increasing the mobility of the polymer chains and acting as a nucleating agent^[10]. The nanoclay is also acting as a nucleating agent, as evidenced when comparing the PNC (0.15), PNC (0.26) and PNC (0.5) curves with the PNC (no oil) curve. Mineral oil is not present in any of these compositions, but the crystallinity in the sample is nevertheless increased with the addition of nanoclay. The maximum crystallinity seen (~6%) was produced by the PNC (oil), PNC (0.26) and PNC (0.79) compositions. This data indicates the potential morphological differences that may be present in the test specimens. It is important to note however that this data was produced using the second heating cycle of the DSC analysis, meaning the amount of crystallization observed does not necessarily correspond to what was present in the molded test specimen. Rather, the second heating cycle ensures that the process history of the sample is erased and emphasizes materials behavior under highly controlled conditions vs. injection molding. Also, the DSC data gives no indication of the orientation of the polymer chains or nanoclay layers. Nevertheless, it is known that orientation effects can dramatically alter mechanical properties.

In this context XRD is able to provide a more in-depth analysis of the microstructure of these materials, assessing both intercalation of the nanoclay and polymer crystallinity. A specific advantage of this method is that it allows for characterization of the morphology of the test specimen as molded.

Figure 7 shows a series of x-ray diffractograms (x-ray intensity versus two-theta angle). The growing peak intensities observed in the 1-10° two-theta range are consistent with the increasing nanoclay concentration in these materials. The spacing between stacked clay layers can be determined using this data as well. As reported by the manufacturer of the nanoclay in question, the d-spacing (distance between the clay layers) is 24.2 Å as-received. In the case of the nanocomposites this increases to approximately 27.6-30.8 Å, which implies that polymer intercalation has occurred. The level of confinement of the intercalated polymer chains is significant, and can lead to local variations in mobility, density, and chain behavior. In contrast, polymer chains sufficiently far from the nanoclay are expected to display bulk-like behavior^[6]. However, since the nanoclay particles act as nucleation sites, nanoclay dispersion can also induce the formation of crystals. The balance between rigid amorphous, mobile amorphous and crystalline polymer, in return, can significantly alter mechanical properties, though the separation of these contributions in this work requires further study.

In addition to providing information on nanoclay dispersion state, Figure 7 also shows sharper and more well-defined peaks appearing at higher angles as nanoclay content is increased. These peaks are associated with polymer crystallinity, and imply that the nanoclay is able to fundamentally alter the microstructure of the as-molded parts from effectively amorphous to (nano)crystalline. While this data does not provide information on orientation or localization of the crystalline material (which might explain skin formation during tensile testing), this is nevertheless a significant finding as far as explaining the properties of these materials are concerned. In particular, this indicates that the optimal amount of crystallinity can improve stiffness, strength and ductility simultaneously in this co-polyester, but that too much crystallinity can have the opposite effect. It is also worthwhile to note that the optimum nanoclay concentration for the realization of these combined improvements in mechanical properties is exceptionally low, not exceeding ~1 wt%. This is an important finding as well, given that this represents the lower end of what most studies consider when studying these materials.

Conclusions

The data shown indicates changes in the morphology of the co-polyester upon addition of nanoclay. In particular, the polymer transitions from a primarily amorphous system to an intercalated system with a small amount of (potentially localized) crystallinity that is nevertheless extremely important in determining mechanical properties. Given the right choice of nanoclay type and content, these results show that the stiffness, strength and ductility of this co-polyester may be improved simultaneously. The orientation of the clay layers and polymer crystals within the system and as a function of location remains unclear, however, and warrants further study, given the possibility for transcrystallinity as demonstrated in nylon nanocomposites^[11] as well as the formation of a skin layer during molding. Other work on nylon nanocomposites has also shown that deformation mechanics strongly depends on dispersion and orientation^[5]. Given this understanding of polymer/clay interactions, some part of the behavior of these systems may be due to orientation effects as well.

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Key words: nanoclay, nanocomposite, co-polyester, mechanical properties

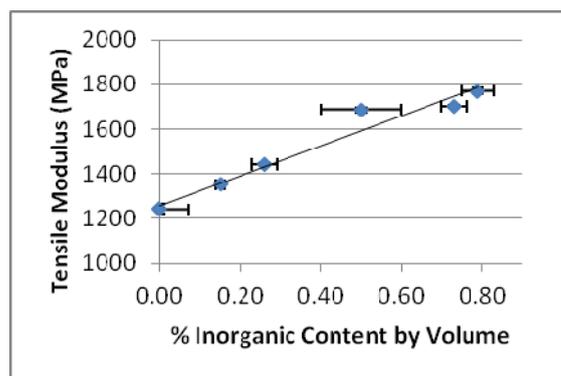


Figure 2. Average tensile modulus of co-polyester nanocomposites vs. inorganic content.

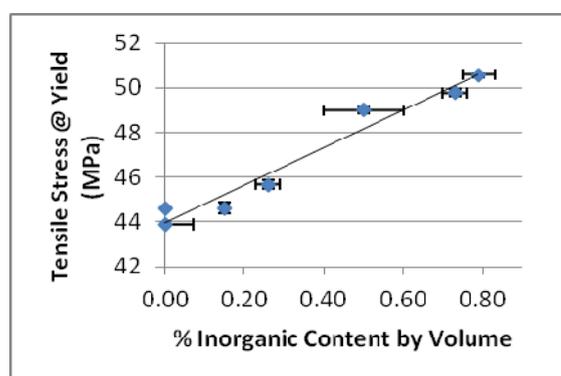


Figure 3. Average tensile stress at yield of co-polyester nanocomposites vs. inorganic content.

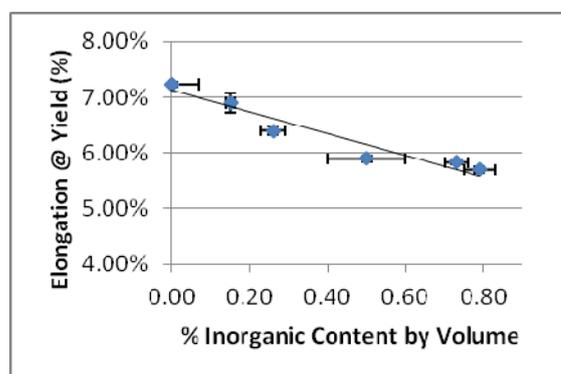


Figure 4. Average tensile elongation at yield of co-polyester nanocomposites vs. inorganic content.

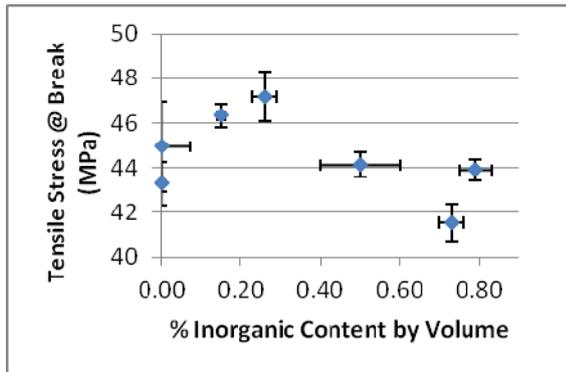


Figure 5. Average tensile stress at break of co-polyester nanocomposites vs. inorganic content.

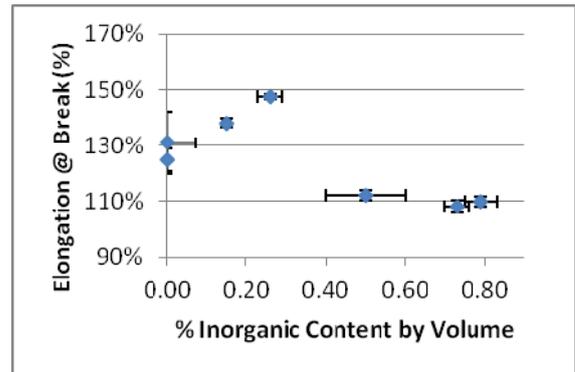


Figure 6. Average tensile elongation at break of co-polyester nanocomposites vs. inorganic content.

Table 5. Summary of DSC data by composition

Compound	Mineral oil	<i>1st cooling cycle</i>			<i>2nd heating cycle</i>			
		T _c (°C)	ΔH _c (J/g)	X _c (%)	T _g (°C)	T _m (°C)	ΔH _m (J/g)	X _c (%)
PNC (no oil)	N	-	-	-	110	247	1.02	0.8
PNC (oil)	Y	198	4.52	3.6	100	241	8.29	6.6
PNC (0.15)	N	204	2.24	1.8	103	243	4.59	3.7
PNC (0.26)	N	199	5.93	4.7	103	241	8.06	6.4
PNC (0.5)	N	201	3.96	3.2	105	244	4.94	3.9
PNC (0.73)	Y	196	6.17	4.9	101	242	6.35	5.1
PNC (0.79)	Y	197	6.95	5.5	103	242	7.78	6.2

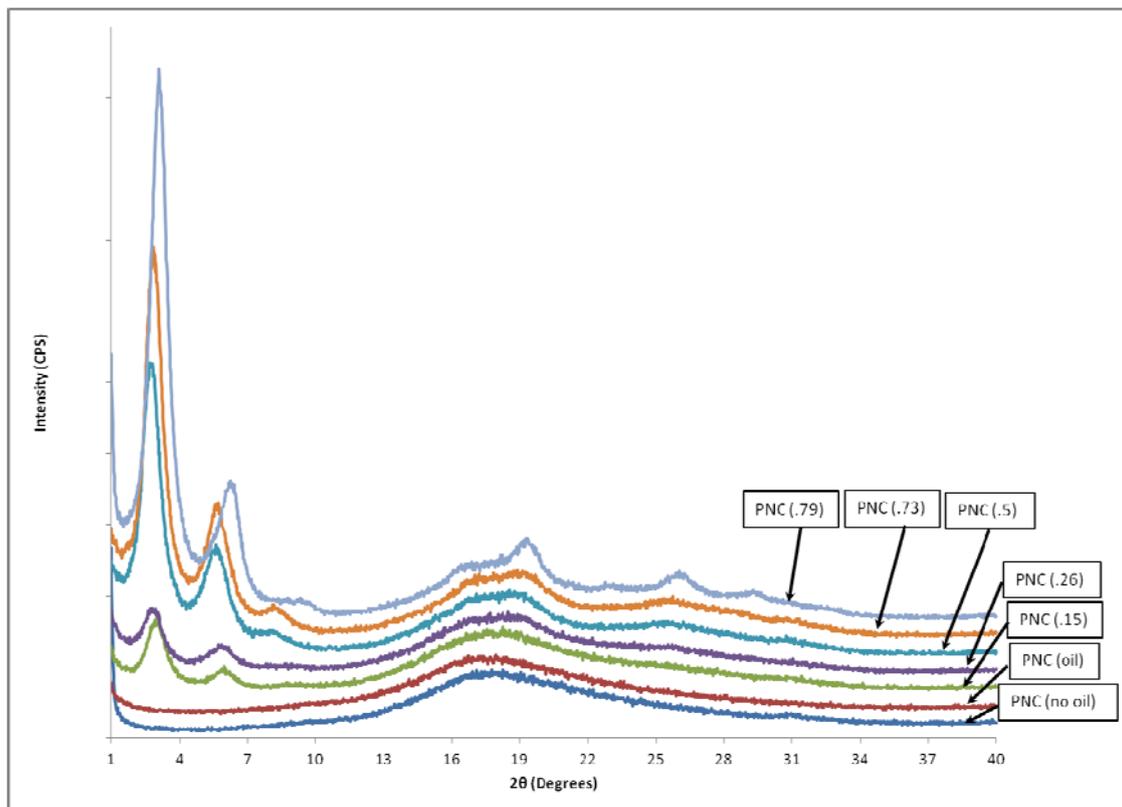


Figure 7. Overlay of raw XRD patterns (shifted vertically for clarity)

PREPARATION OF INTERCALATED ORGANIC/INORGANIC HYBRIDS VIA *IN SITU* SYNTHESIS

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Abstract

Nanostructured organic-inorganic hybrid materials, including polymer nanocomposites, layer-by-layer assembled thin films, have been extensively investigated over the past two decades and have found wide applications owing to their excellent performance. Either regular polymer nanocomposites or layer-by-layer assembled thin films are typically prepared using pre-synthesized nanofillers/nanoplatelets. Here, we report a new approach to prepare nanostructured hybrid materials via *in situ* synthesis of nanoplatelets within the polymer/monomer matrix. Alpha-zirconium phosphate (ZrP) was synthesized in a solution system containing a polymer (such as polyethylene glycol, PEG) or monomer. During the synthesis of ZrP, PEG chains were embedded into the ZrP interlayer space, leading to a larger interlayer distance, which is similar to the intercalated layered compound. Proper formulation ratio proved to be critical to avoid forming pristine ZrP, and avoid interfering the growth of the layered structure of ZrP. It has also been found that longer polymer chains are desirable for minimizing the formation of pristine ZrP, but would not affect the interlayer distance. All the PEG chains are perfectly parallel to the layer planes. Besides polymers, many other molecules have also been successfully embedded into the interlayer space to form an intercalated structure during *in situ* synthesis.

Introduction

Nanostructured organic-inorganic hybrid materials, including polymer nanocomposites, layer-by-layer assembled thin films, have been extensively investigated over the past two decades and have found wide applications owing to their excellent performance.¹⁻⁴ Either regular polymer nanocomposites or layer-by-layer assembled thin films are prepared using pre-synthesized nanofillers/nanoplatelets. For polymer nanocomposites, huge efforts have been made on dispersing nanofillers into polymer matrices, owing to the inherent nature of nanofillers is to agglomerate. However, a desirable state of dispersion is not necessarily achieved. For layer-by-layer assembled thin films, individual nanoplatelets must be pre-formed (exfoliated) before the assembly process.

For most intercalation compounds, they are synthesized by intercalating the preformed layered materials.

Herein, we report a new approach to prepare intercalated polymer-inorganic materials via the *in situ* synthesis of nanoplatelets within the polymer matrix. Alpha-zirconium phosphate (ZrP), $Zr(HPO_4)_2 \cdot 2H_2O$, was selected as the base layered compound to be *in situ* synthesized to prepare intercalated hybrid materials. In this way, polymers/monomers can be incorporated into layered structure during the synthesis process. A uniform intercalated can be formed directly.

Experimental

Materials

Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, 98%, Aldrich), phosphoric acid (85%, Aldrich), and polyethylene glycol (PEG) 400, 600, 1000, 1900, 4000, and 8000 (Alfa Aesar) were used as received

Synthesis

The ZrP based compound was synthesized via a hydrothermal method.⁵ A sample of 20% zirconyl chloride solvent was mixed with pre-determined amount of PEG with various molecular weights and H_3PO_4 with various concentrations in a sealed Teflon-lined pressure vessel and reacted at 100°C for 24 hr. After the reaction, the products were washed and collected by centrifugation three times. After that, the ZrP/PEG compounds were dried at 70°C for 24 hr. The dried samples were ground with an agate mortar and pestle into fine powders.

Characterizations

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer with Bragg-Brentano θ - 2θ geometry (20kV and 5 mA), using a graphite monochromator with Cu $K\alpha$ radiation.

The thermal stability of the ZrP/PEG compounds were characterized by a thermogravimetric analyzer (TGA, TA Instruments model Q50) under an air atmosphere (40 mL/min) at a heating rate of 10°C/min.

Scanning electron microscopy (SEM) images were acquired on a field emission-SEM (FE-SEM) from FEI (Helios Nanolab 400).

Results and Discussion

The synthesis of ZrP has been well investigated. Its morphology, crystallinity, and dimension can be tuned by controlling the synthesis conditions.⁵ Thus, ZrP is an ideal nanoplatelet for the preparation of polymer nanocomposites⁶⁻¹⁷ and intercalation chemistry research.^{9,18,19}

As expected, when PEG was added during the synthesis of ZrP, a PEG/ZrP intercalation compound formed. It is believed that during the grow of ZrP crystals, PEG molecules were embedded into the ZrP layers simultaneously, leading to the formation of an intercalation compound, as briefly illustrated by Figure 1.

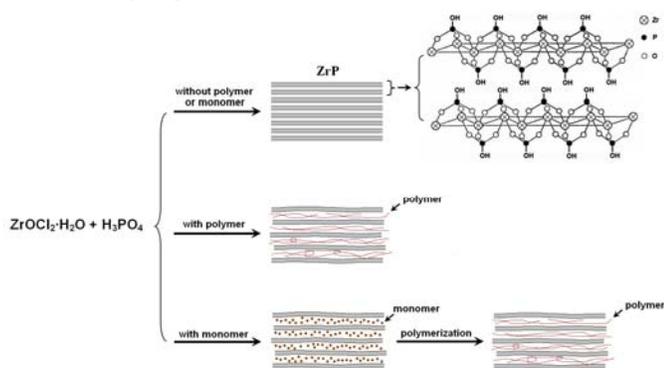


Figure 1. Schematic of the synthesis of ZrP with and without the presence of soluble polymers.

By varying the weight ratio of PEG600 (MW ca. 600) to ZrP in the formulation (assuming all Zr^{4+} cations converted to ZrP) from 25 to 400%, the synthesized hybrid layered materials exhibiting different morphologies and levels of crystallinity, as shown in Figure 2.

When PEG/ZrP ratio is low, the product is a mixture of neat ZrP and PEG/ZrP intercalation compound. With increasing concentration of PEG in the formation, PEG/ZrP intercalation compound begins to dominate. The favored formation of PEG/ZrP intercalation compound over neat ZrP is expected. With a high concentration of PEG molecules in ZrP synthesis environment, statistically such PEG chains will have a high chance to be embedded into the ZrP galleries.

At PEG/ZrP ratio of 200%, a tiny amount of neat ZrP still exists. But when the ratio was further increased to 400%, more neat ZrP was formed, compared to the 200% ratio case. The sample also exhibited reduced crystallinity, as evidenced by the larger peak width and lower signal to noise ratio. This is probably because the crystal growth process of ZrP was significantly interfered by the presence of large concentration of PEG, which can be somewhat considered as a contaminant for the synthesis of ZrP crystals. When the contaminant concentration was relatively low, it was endurable. But if too

much PEG was present, they will negatively affect the formation of ZrP crystal, leading to the observed phenomenon.

While the PEG/ZrP ratio affect the formation of PEG/ZrP intercalation compound as discussed above, the interlayer distance of such intercalation compounds remains to be 10.4 Å. This phenomenon will be discussed later.

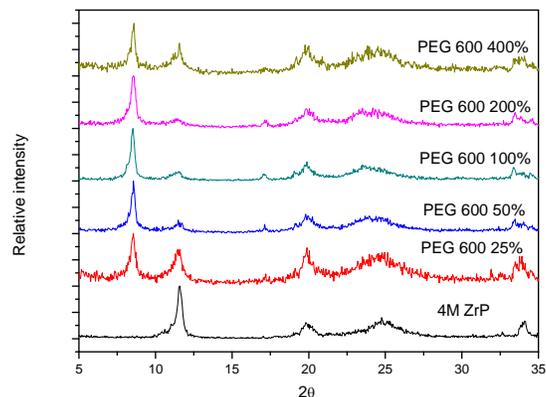


Figure 2. XRD patterns of PEG600/ZrP with various formulation ratios.

When PEG1900 was used during the synthesis of PEG/ZrP intercalation compounds, it was found that much less neat ZrP formed. Even at a PEG/ZrP weight ratio of 25%, only a tiny amount of neat ZrP formed. When the PEG/ZrP weight ratio was raised to 50%, no neat ZrP was detected by XRD, as shown in Figure 3. Again, the interlayer distance of PEG1900/ZrP intercalation compounds remains to be 10.4 Å.

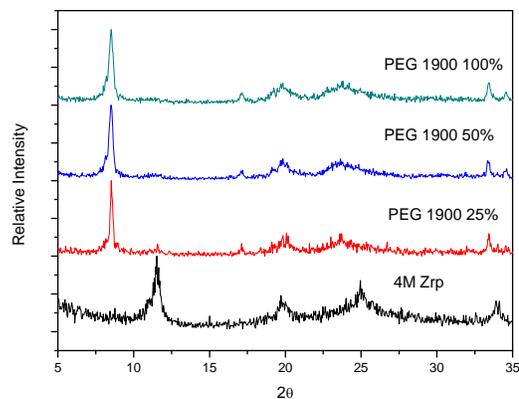


Figure 3. XRD patterns of PEG1900/ZrP with various formulation ratios.

PEG macromolecules with varying MWs were adopted to the synthesis to investigate the effect of polymer chain length on the formation of PEG/ZrP intercalation compounds. The XRD patterns are presented in Figure 4, which show that longer polymer chains are more effective to minimize the

formation of pristine ZrP. While statistically chains with different lengths may have the similar chance to be anchored and embedded within the layers, the longer ones, once anchored, would affect a larger domain of intercalated structure. Thus overall, a longer PEG chain is favorable to help minimize the formation of neat ZrP.

Again, it was observed that the PEG molecules with different chain lengths lead to the same interlayer distance of PEG/ZrP intercalation compounds, which is 10.4 Å. Together with the observation from Figures 1 and 2, it shows that neither the concentration, nor the chain length of PEG, would affect the interlayer distance of the synthesized PEG/ZrP intercalation compounds. This suggests that PEG chains must be perfectly parallel to the layer planes. Simple modeling using Chem3D Pro shows that the PEG chain has a thickness of ca. 2.8 Å. This leads to an excellent agreement with the interlayer distance difference between ZrP (7.6 Å) and PEG/ZrP intercalation compounds (10.4 Å), indicating that only one layer of PEG chains are embedded into ZrP galleries, probably together with some hydration water molecules.

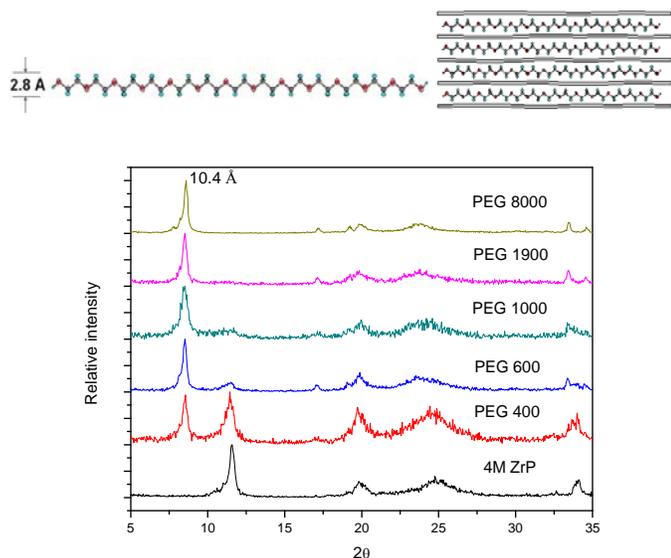


Figure 4. XRD patterns of PEG/ZrP compounds containing PEG with varying MWs at PEG/ZrP weight ratio of 100%.

To further prove that PEG was indeed embedded into the ZrP layers during the formation of ZrP crystals, instead of being intercalated into formed ZrP, a control experiment was carried out and the results were shown in Figure 5. A neat ZrP sample was first synthesized under the same condition to synthesize the above intercalation compounds, whose XRD pattern is shown in Figure 5. Subsequently, 50% PEG (to the synthesized ZrP) was added, and then reacted under the same hydrothermal reaction condition for 24 hours. The final product was collected and dried for XRD. The results show that no PEG was intercalated into the pre-formed ZrP. This proves that PEG cannot be intercalated into ZrP galleries via regular intercalation procedures, which in turn suggests

PEG/ZrP intercalation compounds should be formed as this project designed.

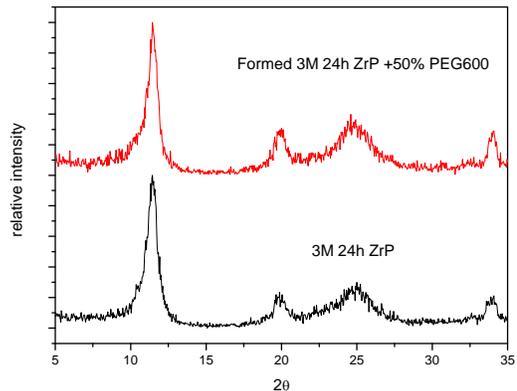


Figure 5. XRD patterns of the sample synthesized from attempted intercalation between ZrP and PEG600.

SEM imaging was performed on selected intercalation samples, which shows that such PEG/ZrP intercalation compounds exhibit a similar size as neat ZrP synthesized under the same conditions. The PEG1000/ZrP intercalation compound exhibited a later dimension of ca. 80 nm (Figure 6), which is consistent with the size of neat ZrP reported before.⁵

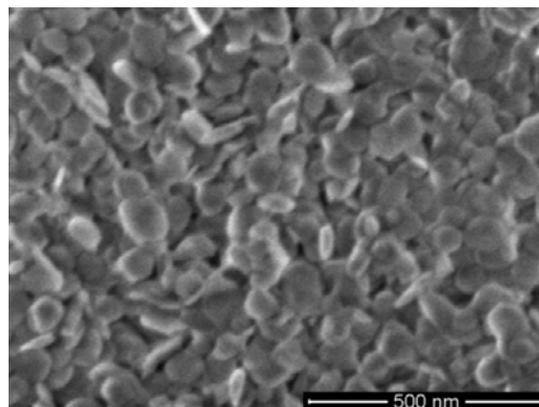


Figure 6. SEM image of PEG1000/ZrP intercalation compound.

Thermogravimetric analyses were also performed on selected intercalation compounds. As shown in Figure 7, the degradation of PEG600 in PEG600/ZrP intercalation compound was slightly delayed compared to the neat PEG600. Such a delayed degradation is believed owing to the insulating effect from the ZrP inorganic layers. The TGA result also suggested that the PEG/ZrP intercalation compound contains ca. 12% PEG.

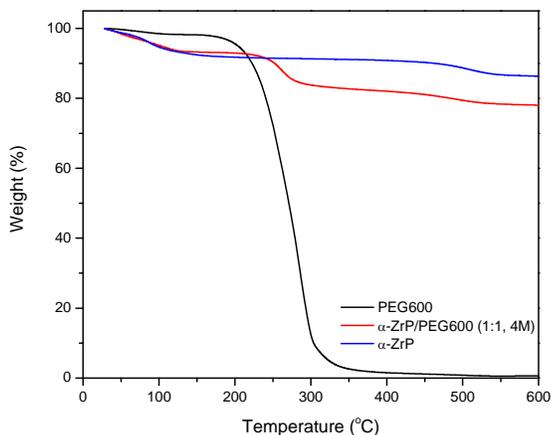


Figure 7. TGA analysis of PEG600, neat ZrP, and PEG600/ZrP intercalation compound.

Conclusions

Overall, the synthesized compounds exhibit a layered structure similar to intercalated ZrP. The increased layer distance is owing to the embedment of PEG in its galleries. Meanwhile, the intercalation compound exhibits a less ordered structure than neat ZrP, which again can be attributed to the existence of guest molecules in the interlayer space, as shown in Figure 1.

The preliminary results have shown that *in situ* synthesis can be an effective and efficient approach to prepared nanostructured composite materials. Other than polymer chains, oligomers, small molecules (such as monomers), or ions, can also be embedded into the interlayer space of layered compounds. Such nanostructured composite materials can not only find applications as regular nanocomposites, may also find applications in sensors, drug delivery, coatings, or as a new platform to study the behavior of polymers which are constrained in layers.

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Key Words

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