TPM&F

Thermoplastic Materials and Foams Division

Communications Excellence Award

Pinnacle Award

TPM&F SCOPE

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

The Society of Plastics Engineers
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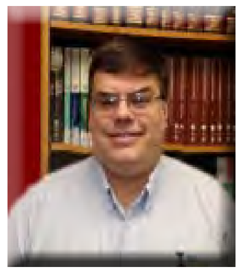
CHAIRMAN'S MESSAGE

OCTOBER 2016



Thanks to the efforts of Xiaoxi Wang and the entire Conference Committee, the 2016 Seattle FOAMS® Conference was a resounding success with 115 attendees, 43 tutorial participants, 47 Boeing tour attendees, 13 new SPE members via registration, and 7 sponsors. The conference program included 23 oral presentations, 2 plenary talks, and 13 student posters. Speakers came from 12 different countries. The Boeing tour was also well received, and we've learned that it is a good practice to stage such visits. The best paper went to Ali Rizvia via Professor Chul Park's live presentation: it was entitled "Fiber-Spun Polypropylene /Polyethylene Terephthalate Microfibrillar Composites with Enhanced Tensile and Rheological Properties and Foaming Ability". What was unique about this paper was the addition of fibrils to greatly improve the melt strength, making it possible to produce foam materials from difficult polymers. We hope to see continued success with the upcoming FOAMS®2017 next October in Germany. Stephane Cousteax has done an excellent job mapping out what will draw people to the TPM&F FOAMS® conferences and in staging the upcoming events through 2020. There may also be some activity in the area of Biopolymer foams area.

On the thermoplastics side, our next shared conference activity will be the Polyolefin 2017 conference. Donna Davis and Anna Azevado will be supplementing this conference with a few TPM&F speaker seasons. This event is scheduled for February 26-March 1st 2017 in Houston Texas. We hope to see you there.

We remain committed to improving our membership value and to improving our Education Outreach to students. Kimberly McLoughlin will be taking over the reins as the Education Chair. The TPM&F Divisions has a number of awards and scholarships that need to be revisited and/or re-

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CHAIRMAN'S MESSAGE (CONTINUED)

vamped, and Kim will be the person leading this activity. On the membership side, we are finding that the best way of getting new members is to put on good conferences and draw them in that way. Nevertheless, Anson is leading a team to contact 450 perspective members in the hopes of converting a few of them to a full TPMF membership status. This year the membership side has also suffered from internal membership system based issues, and we are attempting to recover some of those missing members. To date, roughly 15 have been quickly been added back. We are also contemplating other membership value programs. If any of our members has a good idea how to improve the TPM&F value, feel free to contact me at grove.dale@hotmail.com

Respectfully Submitted,
Dale Grove
TPM&F Chairman

THERMOPLASTIC MATERIALS AND FOAMS DIVISION BEST PAPER WINNERS

FIBER-SPUN POLYPROPYLENE/POLYETHYLENE TEREPHTHALATE MICROFIBRILLAR COMPOSITES WITH ENHANCED TENSILE AND RHEOLOGICAL PROPERTIES & FOAMING ABILITY

Ali Rizvi, Zamil K.M. Andalib, Chul B. Park*
Microcellular Plastics Manufacturing Laboratory, Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario M5S 3G8 (Canada)

ABSTRACT
The in-situ fibrillation of polyethylene terephthalate (PET) in a polypropylene (PP) matrix during conventional fiber spinning of PP/PET (95/5 wt%), enhances the strainhardening behavior in extensional flows of the PP matrix. Furthermore, fibrillated-PET domains increase the tensile strength of PP. Foam extrusion of the microfibrillar composite reveals a two orders of magnitude increase in cell density and a five-fold increase in expansion ratio compared to neat PP. Using fiber spinning of polymer blends to generate microfibrillar composites is technologically promising to improve foaming ability of the matrix polymer.

VISCOELASTIC SHEAR ANALYSIS OF POLYMERIC FOAM MIDSOLES

Alex M. Brill
University of Wisconsin-Madison

ABSTRACT
Athletic footwear companies continually create technological innovations to give athletes a greater running experience. The nonlinear viscoelastic material behavior of polymer foams, found in the shoe midsole, dissipate the ground reaction forces to provide cushioning. Shear analysis up to 50% strain was experimentally conducted at 1 and 5 Hz to characterize the stress-strain performance. Constitutive equations were curve fitted by using Finite Element Analysis performed in ANSYS. A look at footwear industry trends demonstrated the potential for highly-cushioned, low-hysteretic foams to support natural gait movement.

Please see the full papers published within this newsletter – FOAMS® (page 9) and ANTEC®/Thermoplastics Materials (page 14).

BOARD OF DIRECTORS LISTING

THERMOPLASTIC MATERIALS & FOAMS 2016 SCHOLARSHIP AWARD WINNER

Ms. Josey Hrbek

The 2016 year winner of the Thermoplastic Materials and Foams Scholarship award is Ms. Josey Hrbek. Thirteen candidates applied for the scholarship this year, and in the four judges' opinions, Ms. Hrbek emerged as the clear winner.

What attracted us to Ms. Hrbek's credentials were: (i) the wide variety of organizations that she belongs to including SPE, Rho Lambda Panhellenic Honor Society, Gamma Sigma Alpha Honor Society, Tau Beta Pi Honor Society, and Society of Manufacturing Engineers, (ii) her volunteer work in restoring Flint, tutoring other students, and participating in a Sigma Chi Annual Haunted House event which benefited the Huntsman Cancer Research Foundation, and (iii) her outstanding 3.83 GPA which has earned her a variety of Alpha Gamma Delta awards and Kettering University Dean's lists. This is not to mention her broad employment background in paints (PPG), plasma cell technology (Kettering University (KU)), composites (KU), fiber coatings (KU), piping and instrumentation diagrams with AutoCAD (Emergent Biosolutions), and catalytic converting (Umicore Autocat). Josey displays a positive can-do spirit combined with strong initiative, drive, and communication skills which will make her an excellent chemical engineer in the future. We wish her continued success.

The Thermoplastic Materials and Foams Division will continue to offer this scholarship to worthy candidates in the future with the theme of thermoplastic and foam backgrounds. So if you believe that you know of other deserving candidates, please apply in 2017.

Humbly submitted by,
Dr. Dale A. Grove
Thermoplastic Materials and Foams Division
Acting Education Chair

COUNCILOR'S REPORT

The Summer Council meeting was in held from August 20 to 21 in Quebec City, Canada.

The minutes of the last Councilors meeting held during ANTEC® 2016 were approved. An amendment was made to include names of all the attendees in the minutes.

Financial Update by Jeremy Dworshak

Jeremy noted that the Society is not meeting its membership, advertisement and events target for 2016. We are doing a good job in controlling expenses but remain in the red. However, there is an improvement compared to the last year. Wim DeVos, CEO, projected forecast for 2016 year is as shown below.

	Budget	Forecast
Membership	$1,240,000	$1,040,000
Advertisement	$412,000	$280,000

There is a net loss of $50,000.

SPE plans is to increase 'non-due' revenue in the coming years. This year ANTEC® attendance was short by 150 people and that has affected the performance. The operational side will not make the budget. Changing the SPE's business model is important. About 15 years ago, SPE had 30,000 members and now it has dropped to 12,000. In the past, 95% of the revenue came from membership, ANTEC®, and journals.

TopCons offered worldwide are helping with the revenue stream. They also help to reach more people. However, it is shifting income from the SPE HQ to Sections and Divisions.

Wim noted we need new ideas to grow SPE membership. Professional membership dues are $125 but this membership is declining. We have 2000 student members paying $25 annual dues.

Overall membership (which includes E-Members) has grown to over 21,000 members. The data collected from the E-Membership will help with the revenue stream like what Facebook and Twitter are doing. Data will be used to target a select group of advertisers.

Rebates and Membership Dues

Membership dues are changing. The current new membership due is $144 when signing up at TopCon and for renewal it is $129.

- *The proposal is to increase new membership and renewal dues to $155.*
- *New membership dues start January. 1, 2017. An extra income of $200,000 for 2018 is anticipated.*
- *Please note the rebate amount is $10 regardless of annual dues.*
- *A motion was made to increase the SPE membership dues and it was passed.*

India is exception to the rule as there is restriction converting funds collected in the local currency to dollar.

Governance Task Force Model for Governance Reform by Scott Owens

The August Council meeting included approval of several Bylaw & Policy modifications that will transform Society's governance model at the inception of the 2017 Council term. Under the new model, the Executive Committee will be replaced by an Executive Board comprised of functionally qualified and accountable individuals. This board will provide direction and oversight for most Society governance matters, thereby enabling Council to focus on initiatives consistent with key Society objectives, including improving member value, expanding educational programs, etc. Please see new GTF model on the website.

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Bylaws Update by Bruce Mullholland
All the revisions to the Bylaws will become effective immediately instead of waiting for 30 days.
A new member initiation fee is not needed due to all electronic communication. Welcome kits are no longer sent to the new member.

- There were many Bylaw changes as a result of GTF implementation. Some of them are shown below:
- There will be no more appointed Vice Presidents.
- There is now mention of who will be elected by Council and who will be by membership.
- There will be two separate elections.
- Normal majority is now defined in the bylaws.
- Terms of Office: 3 years per new GTF model
- Mention on vacancies and succession are fully described.
- Kept 2/3 majority as presented for bylaw changes and did not change to proposed 'simple' majority.

SPE "Plastics Insight" Updated by Russell Broom
Russell gave a demonstration on Plastic Insight. You can customize enhancements. The tool helps to understand members' interest and demographics.

'The Chain' has several new enhancements which include improved graphics, sampling of current discussion topics, and the introduction of Industry Exchange our newest community supporting general industry awareness. Please note The Chain includes private communities for use by your boards and committees.

Student Chapter
The Imperial College of London was added and the Rochester Section was abandoned.
Several non-compliant Sections include NY, East New England, Akron, Nebraska, Columbia River, Central Europe, and Middle East. The main reason is they have not provided volunteer rosters.
Babli Kapoor, Division Chair, mentioned several non-compliant Divisions including E&E, Thermoforming, and China Extrusions.

Babli Kapoor Perspective on New ANTEC® Model
Babli informed the reason for the decline at ANTEC® is due to competing on-line social & professional avenues and in some cases overlap in the subject matters. ANTEC® has been a strength for the past 74 years. It helps the entire value chain, and is a bridge between industry and academia and global reach.

Suggested Ideas for New Model:
Include lectures on soft skill, career fair, establish a theme, team up with other associations, NPE field trips, STEM activities, and allocate time for Division, SIG and organize activities.
The path forward is to create a new ANTEC® format. Also, create a team that is effective to this cause and connect with Sections/Divisions, create a new blueprint, and target launch in 2018.

Leadership Planning by Scott Owens
We need to develop new society leaders. SPE need diversity on the board along with people who are committed. Any Board member from a Section or Division can serve.

- *Please note anyone can serve in this position*. It does not have to be a Councilor

Scott mentioned how to identify new SPE leaders from a list of 900 people. Leaders need ratings of 3 or higher and for a rating of 7 or 8 for executive committee. Please share this opportunity with your Board members. The plan will be formalized in 30 days and posted on Leadership Lane.

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COUNCILOR'S REPORT (CONTINUED)

Roles & Responsibilities

There will be checks and balances on an annual basis. Individual performances will be reviewed end of the year. For full transparency, we should all review minutes of the meeting, ask questions or concerns. SPE's three-year plan was outlined in a PowerPoint presentation. SPE Membership will elect VP and VP of Technology & Education.

Wim DeVos – Membership Update

Wim noted across the board for Sections and Divisions there is a decrease in membership. He will post ANTEC® attendance and membership history on The Chain.

New Software Demo by Russell Broom

There was a demo done on a new software. It allows understanding who are our members and non-members, heightens that value. New tool tracks members' location, who has joined and who has left. The report will be available to Sections and Divisions. This is a tool connected to the main database. It is a visualization based. This will allow easily welcoming a new member and also connecting with a member who has not renewed. This will be rolled out in October. Membership Chair will receive viewers and the first data set.

The data will be updated monthly and sent to the Membership Chair. It comes as a file with the database, no need to be online. Council will review on this tool during December meeting. In order to make this tool effective, please use the central registration system so it can capture all the data.

ANTEC® Model and Membership

The whole of Council actively participated in two important workshops: improving the ANTEC® and growing Membership. There were many valuable ideas gathered from the effort. The discussions will continue on The Chain on these two important subjects.

Special Interest Group (SIG)

There was a discussion when a SIG should convert into a Division. A recommendation will be made during December's meeting.

HIGHLIGHTS FOR TPM&F BOARD MEETING

Meeting Date: September 13, 2016

Minutes compiled by Maxwell Wingert

ATTENDANCE

Attending the BOD meeting in person: *Dale Grove, Xiaoxi Wang, Theresa Healy, Stephane Costeux, Changchun (Chad) Zeng, Maxwell Wingert, Gary Wilkes, Masahiro Ohshima, Shu-Kai Yeh, Peter Schroeck, Eric Teoh, Anson Wong, Kim McLoughlin, Hani Naguib, Aaron Guan, Chul Park, Miguel Rodriguez-Perez* **Attendence via phone:** *N.S. Ramesh, Donna Davis, Perry Vadhar*

CHAIR REPORT – Dale Grove

Dale reminded all of us about SPE's anti-trust and conflict of interest policies. He thanked everyone for their time in joining this meeting. Kim McLoughlin and Shu-Kai Yeh are the newest TPM&F board members. Congrats to both. Shu-Kai Yeh became a member directly after the election, while Kim was appointed on to the committee due to some open board positions. We need SPE HQ to update the records as well as the TPM&F website. The Pinnacle and Communication Excellence Award applications are both due in January 2017. There was some discussion about the rebate system and Dale had to table that until further review takes place soon. s.

COUNCILOR CHAIR REPORT – Perry Vadhar

(see page 13-14 in this newsletter issue)

MEMBERSHIP REPORT – Anson Wong

ANANDA CHATTERJEE TRAVEL AWARD 2016

- Two rounds of two $500 awards are set for 2016
- The first round has been completed. There were 8 applicants and six judges. The two winners were:
  - Alireza Tabatabaei-Naeini *(University of Toronto)*
  - Syed Hassan Mahmood *(University of Toronto)*
- The second round is targeted for late 2016.

FOAMS® COMMITTEE REPORT – STÉPHANE COSTEU Stéphane proposed having the FOAMS® 2017 Conference in Germany. There was some concern as to who would be the Treasurer without local support. There was discussion to have someone from the board as the Co-Chair and to gain

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support from SPE Europe. There was a suggestion to have Chul serve as the Co-Chair with Hani's assistance. After Stéphane got some additional information from SPE as to how such a conference would run and as to how the European part of SPE would assist, there was a later email motion to have this location in Germany. The motion was approved. It appears that the date is going to be the week of October 9, 2017.

FOAMS® COMMITTEE REPORT – Xiaoxi Wang/ Vipin Kumar/ Stéphane Costeu Xiaoxi will send a report out once this conference is over. So far, 13 new TPMF members were achieved thanks to the conference. Overall there were 105 attendees, 46 who went on the Boeing tour, and 44 tutorial attendees. There were 7 sponsors: 1 Gold, 2 coffee break, and the rest exhibitors. There was some discussion about the TPM&F equipment being outdated *(i.e.; projector, laptop, and telecom)*. The division should invest in a new projector for conference since the ten year old one has broken.

- Reedy Scholarship Awards – The winners were: Victoria Bernardo Garcia, University of Valladolid and Syed Hassan Mahmood, University of Toronto.
- Best Paper Award– Gary Wilkes is all set and has his volunteers.
- Poster Award– Poster are all ready to be displayed.

EDUCATION CHAIR REPORT – Dale Grove (acting) Dale is the acting Chair for this committee. However, Kim will take this role over going forward with Dale's support.

- Scholarship Award - This area must be revamped and advertised since many members are not aware of it.
- Platinum SAC Level - Will be reviewed and discussed. Travel awards and scholarships need names.
- PlastiVan and Community Outreach – There must be more activity in this area. The Seattle area has done it the last few years.
- New Chair Appointment-The next Education Chairperson will be Kim McLoughlin.

ACTION: D. Grove will write a standard operating procedure and hand it off to Kim.

COMMUNICATION CHAIR REPORT – Theresa Healy

Website The website is current. Please review (www.spetpmf.com) and send updates. Once the FOAMS® Conference is over, the Polyolefins Conference will be advertised. The BOD list needs to be updated by the end of September.

Linked- In TPM&F site This has been updated and checked daily for new members. There was an announcement made on this page to remind people to register for FOAMS®. Discussions and posts will continue to take place. The site should be informative as well as a place for networking. It will continue to be used to promote conferences, technical information, and webinars.

INTERNATIONAL ACTIVITIES REPORT – Hani Naguib/Miguel Perez/Masahiro Ohshima

Shaayegan, V., Park, C.B., Franco, C., and Han, S., "Experimental Studies in Microcellular Injection Molding", CONNECT! European Moldflow User Meeting 2016, Frankfurt, Germany, June 21-22, 2016

Cherukupally, P., Farnood, R., Hinestroza, J.H., Bilton, A.M., and Park, C.B., "Adsorption Mechanisms of Emulsified Crude Oil Droplets onto Hydrophilic Open-Cell Polymer Foams", 32nd International Conference of the Polymer Processing Society, Paper # S16-388, Lyon, France, July 25-29, 2016

Kazemi, Y., Ramezani Kakroodi, A., Wang, S., Ameli, A., Filleter, T., and Park, C.B., "Electrical Conductivity and Crystallization Behavior of Polypropylene in the Presence of Supercritical Carbon Dioxide and Multiwalled Carbon Nanotubes", 32nd International Conference of the Polymer Processing Society, Paper # S02-592, Lyon, France, July 25-29, 2016

Liao, X., Xu, H., Bai, J., Yang, Q., Li, G., and Park, C.B., "Effects of Viscoelastic Properties on the Foam Morphology of Silicone Rubber Using Supercritical Carbon Dioxide", 32nd International Conference of the Polymer Processing Society, Paper # S05-199, Lyon, France, July 25-29, 2016

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Ramezani Kakroodi, A., Kazemi, Y., Ding, W.D., Ameli, A., and Park, C.B., "The Effects of Morphological Manipulations on the Characteristics of Polylactic Acid (PLA)/Nanofibrillar Nylon-6 Blends", 32nd International Conference of the Polymer Processing Society, Paper # S06-120, Lyon, France, July 25-29, 2016

(keynote) Shaayegan, V., Wang, G., and Park, C.B., "The Effect of Melt/Gas Mixture Compressibilty on the Cell-Nucleation Behaviors in High-Pressure Foam Injection Molding", 32nd International Conference of the Polymer Processing Society, Paper # S05-48, Lyon, France, July 25-29, 2016

Shaayegan, V., Cuif, L., Ameli, A., Wang, S., and Park, C.B., "Investigation of Fiber Orientation and Displacement in High-Pressure Foam Injection Molding of Polystyrene/Carbon-Fiber Composites", 32nd International Conference of the Polymer Processing Society, Paper # S02-133, Lyon, France, July 25-29, 2016

*Theresa will post these activities and papers to our website.

NEW AND OLD BUSINESS

Chul mentioned there was a BIOFOAMS Conference that he was Chairing, but he suggested that the TPM&F Division consider taking this over. This could be a separate Topcon. Chul has been alternating with another person. Chul will work on a write up to send the BOD members to see if this is of interest, and Kelvin Okamoto was recommended as a point of contact.

Stephane asked whether Chair travel funding should be an on-going budget item. After some discussion, it was decided that this should be done on an individual case by case basis since in most cases an incoming Chair will have travel funds. The reason why this was deemed necessary in this one particular case was because the present Chair's company restricted travel during his mid-tenure.

Adjourn-Meeting was adjourned at 8:28pm Pacific Time.

NEWSLETTER PUBLICATION SPONSORSHIP INFORMATION

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If you are interested in sponsorship in our newsletter, please contact:

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FIBER-SPUN POLYPROPYLENE/POLYETHYLENE TEREPHTHALATE MICROFIBRILLAR COMPOSITES WITH ENHANCED TENSILE AND RHEOLOGICAL PROPERTIES AND FOAMING ABILITY

*Ali Rizvi, Zamil K.M. Andalib, Chul B. Park**

Microcellular Plastics Manufacturing Laboratory, Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario M5S 3G8 (Canada)

Abstract

The in-situ fibrillation of polyethylene terephthalate (PET) in a polypropylene (PP) matrix during conventional fiber spinning of PP/PET (95/5 wt%), enhances the strain-hardening behavior in extensional flows of the PP matrix. Furthermore, fibrillated-PET domains increase the tensile strength of PP. Foam extrusion of the microfibrillar composite reveals a two orders of magnitude increase in cell density and a five-fold increase in expansion ratio compared to neat PP. Using fiber spinning of polymer blends to generate microfibrillar composites is technologically promising to improve foaming ability of the matrix polymer.

Introduction

The use of PP for foaming applications is restricted because it generally exhibits inadequate rheological properties at processing temperatures. Unlike amorphous polymers, PP shows a rapid change in viscosity and melt strength around the melting temperature. Therefore, accessing the processing temperature window for generating stable foams, where the polymer is stiff enough to prevent cells from rupturing but also soft enough to deform under relatively small stresses during bubble growth, is challenging.

Although chemical crosslinking of polymers is an effective strategy for increasing their melt strength and strain hardening response in extensional flows, the approach is undesirable as it renders the polymer difficult to process and recycle. [1, 2] Long-chain branching is also effective in increasing the melt strength and strain hardening behavior of polymers but the cost of such resins is several folds higher than their linear counterparts. For example, long chain branched PP is effective in producing low density foams of PP, however, commercially available high *melt strength* PP is at least twice as expensive as linear PP. [3, 4, 5] Incorporating organically modified layered nanosilicates have been effective in improving the melt viscosity and tensile stress growth of polymers strain hardening during extension in processes such as foaming. This has translated into improvements in cell morphology of the foams, but the highest enhancement in cell morphology can only be realized when the nanosilicates are dispersed uniformly

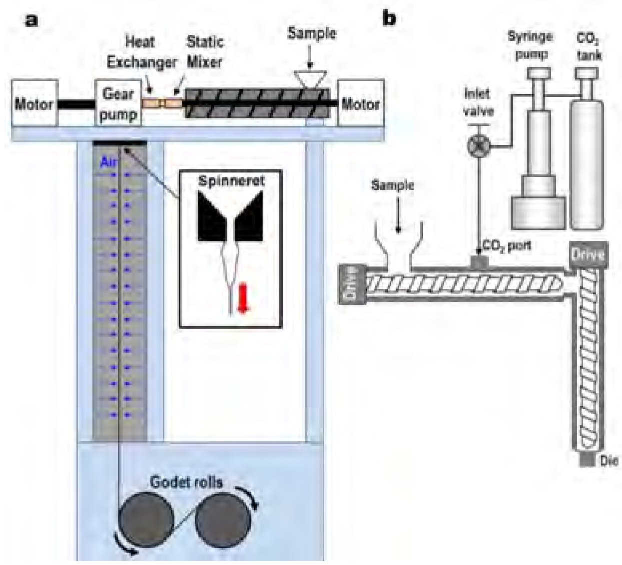

Fig. 1 Schematics of a) the custom-built fiber spinning system used in the study; b) the custom-built tandem foam extrusion system used to prepare foams.

(exfoliated). [6, 7] Although highly desirable, exfoliation of nanosilicates in non-polar polymer matrices is challenging and requires fine tuning of the clay surface chemistry as well as its synthesis and processing conditions. [8, 9, 10] Despite the availability of a number of methods to compensate for the weak tensile stress growth during extension of low melt strength polymers, it still remains a challenge to produce their foams with a high cell density and high expansion ratio. The deficiencies of these existing strategies call for a need to develop methods to improve the foaming ability of semicrystalline polymers in an environmentally-sustainable, inexpensive, and completely scalable process.

In earlier investigations, we found that the incorporation of flexible polymer fibers can improve the melt strength and strain hardening behavior of a polymer matrix in extensional flows. Above a threshold concentration, typically around 3 to 5 wt%, the long aspect ratio fibers form entanglements creating a physical network which resists breakage in the melt. When this polymer-fiber system, known as a *microfibrillar composite,* is stretched, the network of entangled fibers cannot disentangle readily enough to follow the deformation. This inability to disentangle is believed to be the origin of strain-hardening. Using a small-scale microcompounder we demonstrated improvements in these properties for microfibrillar composites of polyethylene (PE)/PP, and PP/PET. While these investigations were effective proof-of-concept experiments, the materials were prepared on a small-scale microcompounder which did not scale up to manufacturing volume twin-screw extruders because equipment design attributes and processing parameters were fundamentally different. Thus, the microfibrillar composites of these materials could not be prepared using a large-scale twin-screw extruder.

In this study, we demonstrate that large scale production of microfibrillar composites of PP/PET can be accomplished through conventional fiber spinning. Fibrillation of PET domains during fiber spinning is attributed to two factors: 1) the transverse contraction and longitudinal elongation in the spinneret die, and 2) the extension caused by cold-drawing performed using the godet. The microfibrillar composite prepared using fiber spinning shows improvements in solid-state mechanical properties such as tensile properties, and rheological properties such as strain-hardening in extensional flows. Foam extrusion conducted using the microfibrillar composite and CO_2 as the foam blowing agent reveals a two orders of magnitude increase in cell density and a five-fold increase in expansion ratio compared to neat PP. The increase in cell density in the microfibrillar composite is attributed to the concurrent increase in strain-hardening behavior during extension, and fiber-induced stress variations which facilitates nucleation of CO_2 bubbles. The increase in expansion ratio in the microfibrillar composite is attributed to the strain hardening response which prevents cell wall rupture preventing CO_2 loss.

Experimental

Materials: The matrix polymer employed in this study is a poly(propylene-co-ethylene) random copolymer (PP) commercially available as Sabic® PP 670K with a melt flow index (MFI) of 10 g/10 min at 230 °C/2.16 kg. The dispersed phase polymer employed in this study is polyethylene terephthalate (PET) copolymerized with 3.5 % 1,4-cyclohexanedimethanol (CHDM), commercially available as Eastapak® PET 9921 (M_n =26 000 g mol^{-1}). Carbon dioxide (CO_2) is purchased from Linde Gas with purity in excess of 99%. Xylene is purchased from Caledon Labs and used as received.

Fiber Spinning: Blends of PP/PET (95/5 wt%) are prepared in a Leistritz co-rotating twin-screw extruder with a screw diameter of 27 mm and an aspect ratio of 40. The extrudate is shaped into a cylindrical strand, led into a water bath and pelletized using a pelletizer. The resultant blend shows well dispersed spherical domains of PET in the PP matrix as shown in **Fig. 2a.** Fiber spinning of the PP/PET (95/5 wt%) blend prepared in the twin-screw extruder is conducted on a custom-built fiber spinning system shown in **Fig. 1a.** The PP/PET (95/5 wt%) blend is fed into the hopper of the fiber spinning system which comprises of a 19 mm single screw extruder. The temperature of the extruder barrel is maintained at 237 °C. The extruder screw speed is set to 15 rpm. An Omega FMX-84441-S six element static mixer with a diameter of 6.8 mm and a Labcore H-04669-12 heat exchanger are positioned downstream to the extruder. An Oerlikon Barmag ZP504-0-IZ gear pump is attached after the heat exchanger to regulate the melt flow before it reaches the spinneret. The gear pump speed is maintained at 15 rpm. The spinneret comprises of a capillary die with a diameter of 0.6 mm and a length of 3.6 mm. As the extrudate exits the spinneret, it passes through a cross-flow ventilation system which cools the fiber before it comes in contact with the draw rolls, known as godets. The rotational motion of the godet draws the extrudate. By controlling the rotational rate of the godet, the extrudate draw ratio can be controlled. The draw ratios studied are 10.2:1 and 20.4:1. For comparison, an undrawn sample which has passed through the spinneret but not drawn by the godet, is also studied.

Measurements: The tensile strength and elongation of fiber-spun single fibers is measured using an Instron 5847 microtester equipped with a 50 N load cell in accordance with ASTM D3822. Measurements of uniaxial extensional viscosity are made using an Extensional Viscosity Fixture (EVF, TA Instruments) attached to an Advanced Rheometric Expansion System (ARES). The samples are tested at strain rates from 0.01 to 1 s^{-1} and at a sample environment temperature of 170 °C.

Foam Extrusion: A tandem foam extrusion system similar to those employed by the foam manufacturing industry is used to foam the samples. The tandem foam system comprises of two single-screw extruder barrels. The first extruder is a 5 horsepower (hp) Brabender 05-25-00 consisting of a mixing screw with a diameter of 19 mm and an aspect ratio of 30. The second extruder is a 15 hp Killion KN-150 consisting of a mixing screw with a diameter of 38.1 mm and an aspect ratio of 30. **Fig. 1b** gives a schematic of the configuration of the extrusion system. A metered amount of CO_2 gas is injected into the melt through an injection port positioned at the first extruder. The lack of tumbling motion for the as-spun fibers prevents these materials from being pushed forward by the single screw of the tandem foam extrusion system. Therefore, the diameter of the fiber-spun materials is increased to approximately 2 mm by making the samples pass through a capillary die attached to a twin-screw extruder at a temperature of 170 °C. The PET domains remain in solid-state during this process and retain their fiber-like morphology. The cylindrical strands of 2 mm diameter are led into a water bath and pelletized. The pelletized blends are able to tumble and thereby flow in the feeding zone of the single-screw foam extrusion

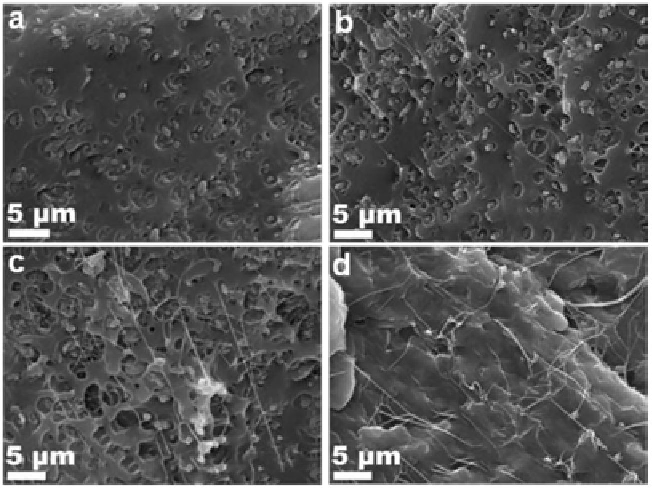

Fig. 2 PP/PET (95/5 wt%) blend morphology of, a) melt-blended PP/PET in a twin-screw extruder; b) undrawn PP/PET where the PP/PET blend in a) is pumped through the spinneret but not drawn; c) fiber-spun PP/PET drawn at a draw ratio of 10.2:1; d) fiber-spun PP/PET drawn at a draw ratio of 20.4:1.

system. The first extruder barrel of the foam extrusion system is maintained at 170 °C. 7 wt% CO_2 is injected into the first extruder barrel at a constant flow rate using a syringe pump. We employ a brass capillary die comprising of a circular pinhole with a diameter of 1.2 mm and a channel length of 10 mm. The temperature of the second extruder barrel and the die is brought down and the foamed samples are collected at each set temperature only after the system temperature has equilibrated. The foam volume expansion ratio, $\varphi = \rho/\rho_f$ is calculated where ρ and ρ_f are the mass densities of samples before and after foaming, respectively, determined using the water displacement method according to ASTM-D792. Additionally, the number of bubbles per unit volume, called the cell density, is also calculated using SEM images of the foams.

Results and Discussion

Fig. 2a shows the morphology of twin-screw extruded PP/PET before fiber spinning. The PET exhibits no evidence of fibrillation and exists as well dispersed, isolated domains in the PP matrix. **Fig. 2b** shows the morphology of PP/PET after pumping the blend through the spinneret of the fiber spinning equipment without drawing. Some degree of fibrillation is noticed and captured in the electron micrograph due to the transverse contraction and longitudinal extension in the spinneret. **Fig. 2c** shows the morphology of fiber spun PP/PET after drawing at a draw ratio of 10.2:1. A larger degree of fibrillation is observed here due to the additional extensional flow contributed by drawing. **Fig. 2d** reveals that when the draw ratio is increased to 20.4:1, the PET

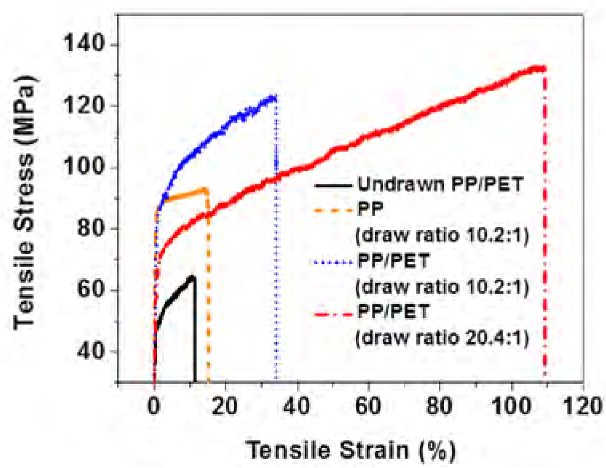

Fig. 3 Tensile stress-strain behaviour of fiber-spun PP/PET (95/5 wt%) drawn at draw ratios of 10.2:1 and 20.4:1. For comparison, the tensile stress-strain behaviour of neat PP drawn at a draw ratio of 10.2:1, and undrawn PP/PET is also included.

domains are almost completely fibrillated. The average fibril diameter is 210 nm, and the average fibril length is 38 µm. Thus, the aspect ratio is about 181. High aspect-ratio fibrils are known to contribute substantially towards the solid-state mechanical properties and the rheological properties of the matrix polymer. Consequently, we investigate the solid-state tensile properties and the uniaxial extensional viscosity of the as-spun microfibrillar composite.

Fig. 3 shows the tensile stress-strain properties of undrawn PP/PET (95/5 wt%) shown in **Fig. 2b**, drawn PP/PET (95/5 wt%) at the draw ratios of 10.2:1 and 20.4:1 and neat PP drawn at 10.2:1. While the tensile strength of neat undrawn PP is known to be about 30 MPa, [11] the tensile strength of fiber-spun PP is 90 MPa. This increase in tensile strength after fiber-spinning the PP is due to an oriented crystalline morphology known as the *shish-kebab* structure. [11, 12] During fiber spinning, PP chains are highly extended and orientated in the direction of drawing prior to crystallization. When crystallization initiates, lamella grow normal to the direction of drawing. This crystalline phase and degree of orientation are responsible for the improved tensile strength. [11]

The tensile stress-strain behavior of undrawn PP/PET fibers shown in **Fig. 2b** is found to be worse than PP fibers due to the poor interfacial adhesion between the PP matrix and the PET domains. [13] When PP/PET is fiber spun, higher ultimate tensile strength and larger elongations at break are observed and the increase is dependent upon the draw ratio. For example, PP/PET fibers drawn at a draw ratio of 10.2:1 show an ultimate tensile strength of 123 MPa and an elongation at break of 34% whereas PP/PET fibers drawn at a draw ratio of 20.4:1 show an ultimate tensile strength of 132 MPa and an elongation at break of 109%. We attribute the

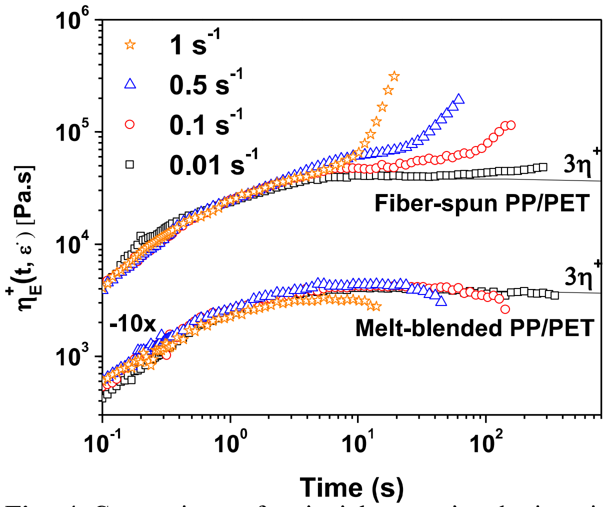

Fig. 4 Comparison of uniaxial extensional viscosity of PP/PET before and after fiber spinning at a draw ratio of 20.4:1.

enhanced mechanical performance of our fiber-spun PP/PET to the PET-assisted formation of *shish-kebab* structures in the PP matrix as reported previously, [14] which improves the stress transfer from the matrix to the fibrils.

Fig. 4 illustrates the uniaxial extension viscosity, at various extensional strain rates, for the microfibrillar composite shown in **Fig. 2d**. For comparison purposes, the uniaxial extensional behaviour of melt-blended PP/PET (95/5 wt%) is also included (shown in **Fig. 2a**), where the PET exists as well dispersed isolated domains. The solid line in the figures represents the linear viscoelastic prediction of extensional viscosity, [15] obtained from startup shear experiments at a strain rate of 0.001 s^{-1}. The uniaxial extensional flow behaviour of melt-blended PP/PET is similar to that of linear PP, and no strain hardening is observed over the strain rate scale studied (0.01 to 1 s^{-1}). In contrast, the fiber-spun PP/PET exhibits a pronounced strain-hardening behaviour in uniaxial extensional viscosity measurements at strain rates higher than 0.1 s^{-1}. These high aspect ratio PET fibrils are able to form a network structure through physical entanglements. In response to an extensional flow, the network of fibrils is not able to disentangle readily enough to follow the deformation and strain hardening is observed. [16, 17] Since strain hardening in uniaxial extension is expected to have implications on polymer foaming, in the subsequent section we investigate the foaming behavior of the microfibrillar composite.

Extrusion foaming is conducted on the melt-blended PP/PET (95/5 wt%) shown in **Fig. 2a**, microfibrillar composite of PP/PET (95/5 wt%) prepared at a draw ratio of 20.4:1 shown in **Fig. 2d**, and fiber-spun PP treated with the same processing history as the fiber-spun PP/PET. **Fig. 5a** shows the cell structure of these three samples at three different die temperatures (140°C, 145°C and

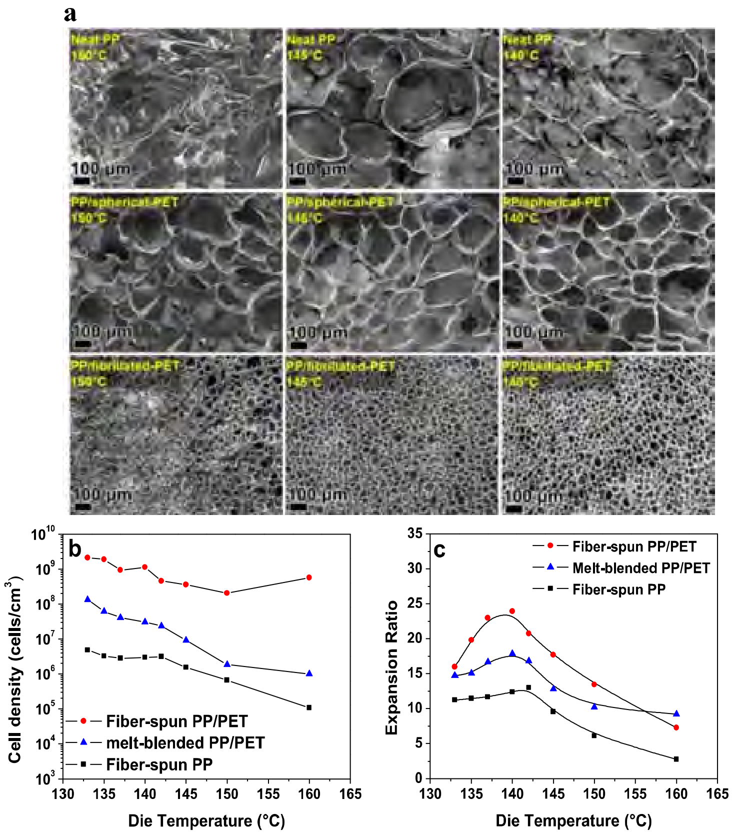

Fig. 5 Characterization of the foam morphologies from melt-blended PP/PET, and microfibrillar PP/PET prepared at a draw ratio of 20.4:1. For comparison purposes the foam morphologies of PP that has undergone the same thermal and processing history as the microfibrillar composite is also included: a) SEM micrographs of foams obtained after foam extrusion at different temperatures; b) cell density as a function of the die temperature for the three samples; c) Foam volume expansion ratio as a function of the die temperature for the three samples.

150°C). A decrease in the cell size and an improvement in the uniformity of the foam structure can be observed at the studied temperatures in the following order: neat PP < melt-blended PP/ PET < microfibrillar composite of PP/PET.

To quantify this improvement in the foam structure, the cell density and the foam expansion ratio are calculated as a function of the extrusion die temperature. **Fig. 5b** shows that the cell density of the microfibrillar composite is up to two orders of magnitude higher than neat PP. The improved cell density is due to the presence of the solid-state PET fibers which act as heterogeneities and induce microscopic stress variations inside the polymer matrix, thereby decreasing the energy barrier for cell nucleation. [18, 19, 20, 21] The strain hardening in an extensional flow observed for fiber-spun PP/PET also influences the cell density by reducing the cell-deterioration mechanisms such as cell coalescence. [22]

Fig. 5c shows that the foam volume expansion ratio of the microfibrillar composite is highest among the three materials studied. Up to a five-fold increase in expansion ratio is seen compared to neat PP. The foam volume expansion ratio is a measure of the degree of gas retention within a foamed polymer. [23] A high expansion ratio indicates gas escape from the polymer is inhibited. The noticeable enhancement in the expansion ratio for the microfibrillar composite is attributed to the strain hardening response exhibited by the fiber-spun PP/PET which prevents cell-wall rupture during cell growth due to the viscosity increase with strain. The observed enhancement in the foaming ability is consistent with the previous reports on foam extrusion of polymer-fibrillar blends where the *in-situ* generation of polytetrafluoroethylene (PTFE) fibrils in a PP matrix led to similar enhancements in both expansion ratio and cell densities. [22, 24]

Conclusions

Fiber spinning is a feasible approach to preparing microfibrillar composites. For the case of PP/PET microfibrillar composites, PET fibers improved the tensile strength, and strain hardening in uniaxial extensional flow of the PP matrix. Extrusion foaming experiments revealed that the presence of the PET fibrils in PP improve cell density by up to two orders of magnitude and expansion ratios by up to five-folds. The proposed strategy of using conventional fiber spinning to produce microfibrillar composites is technologically promising for improving the foaming ability of difficult-to-foam-plastics.

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VISCOELASTIC SHEAR ANALYSIS OF POLYMERIC FOAM MIDSOLES

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Abstract

Athletic footwear companies continually create technological innovations to give the athlete a greater running experience. The nonlinear viscoelastic material behavior of polymer foams, found in the shoe midsole, dissipate the ground reaction forces to provide cushioning. Shear analysis up to 50% strain was experimentally conducted at 1 Hz and 5 Hz to characterize the stress-strain performance. Constitutive equations were curve fitted by using Finite Element Analysis performed in ANSYS. A look at footwear industry trends demonstrated the potential for highly cushioned and linear foams to support natural gait movement.

Introduction

The athletic footwear industry increased rapidly from corporations grasping the emerging running trend beginning in the 1970s. Nike and Adidas were among the top sports footwear manufacturers to distribute revenue into research and development promising a greater running experience and increased injury prevention. These claims continue today grounded by their dynamic technological development of the midsole region of the shoe, which is the main damping mechanism of the foot-ground interaction during running applications [1, 3, 5]. The major part of the midsole is comprised of a foam polymer, but is often coupled with other cushioning technologies, such as air pouches, thermoplastic support shanks, and non-Newtonian fluids. However, the injury rate remains unchanged [2]. The footwear engineer must be knowledgeable in the studies of human running motion to provide design decisions to reduce injury due to impact loads.

Ethylene-vinyl acetate (EVA) has been the industry leading material, providing durability and toughness over a wide temperature range, along with water resistance, and inexpensive manufacturing. Polyurethane (PU) is also used in running shoes for areas needing greater strength and durability due to the aging resistance [3]. PU is denser than EVA, so it is often placed in high impact areas of the midsole to control the medial rotation of the ankle joint, also referred to as pronation [4]

Kinematic trends show highly cushioned shoes increase vertical loading rate and significantly decrease peak lateral force than footwear with moderate foam thickness [6]. Authors suggest highly cushioned shoes could reduce pronation due to the decrease shear impact forces. However, biomechanical research on barefoot running has proven that runners increase impact-moderating behavior as the reduction in plantar shear movement, perceived as foot stability, increases. The force production remains similar to shod cases, however running efficiency increases due to proprioception (neural-mechanical adaptation to perceive ground contact) by enhancing the storage and restitution of elastic energy in the ankle extensors [7]. The sports footwear engineer must understand the responsiveness and energy dissipating properties of foam materials in shear to accurately predict performance measures, such as metabolic efficiency and joint rotation.

Materials and Procedure

Two polymeric foams found in commercially available high performance running shoes were analyzed. Nike Cushlon™ Ethylene Vinyl Acetate (EVA) foam is compared to Adidas Boost™ expanded thermoplastic polyurethane (E-TPU) foam. Both materials are steam compression molded from hundreds of small foam granules [8]. This process increases the responsiveness, while decreasing the density. EVA is an open-cell foam, while E-TPU is a closed cell foam.

Mechanical Analysis

Viscoelasticity is the contribution of two forces in a system: the elastic solid and the viscous liquid. A sinusoidal input displacement results in a phase lag of the resulting stress response of the material, indicating an energy loss. Lissajous loops provide a representation for the viscous dissipation during a dynamic strain input, as seen in Figure 1 [9].

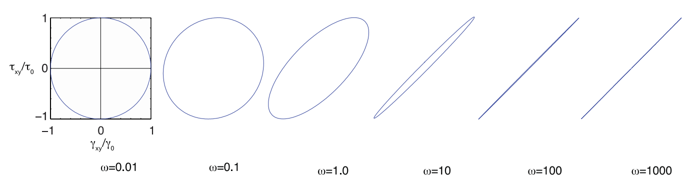

Figure 1: Lissajous loops showing a decrease in energy loss from low frequency input (100% viscous) to high frequency input (100% elastic).

The area inside the loop is the energy dissipated by the material. Literature analysis of footwear foams test the uniaxial compression, since the compressive direction

 (CONTINUED FROM PAGE 9)

accounts for roughly 80% of the force contribution during running applications [5, 11, 12]. Typical stress-strain behavior can be seen in Figure 2. Large deformation of the foam demonstrates three regions: linear elastic, plateau or collapse, and densification. During low strains, the foam cell walls bend to allow a linear reaction before large deformations buckle the cell walls to reach a plateau of the stress response. Finally, there is a region of densification where the stress increases sharply and the foam acts as a solid polymer.

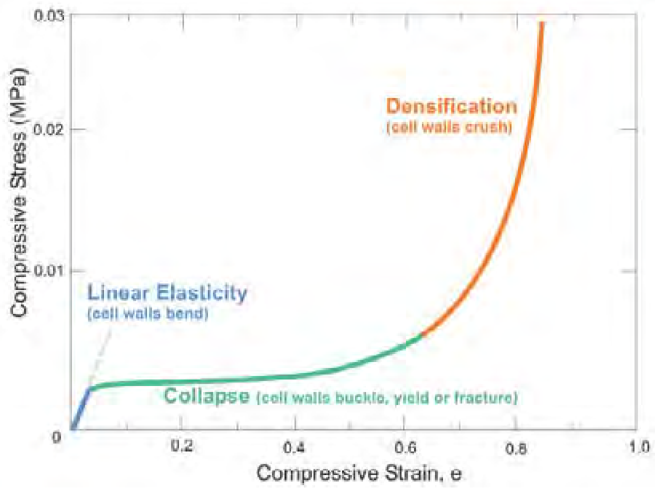

Figure 2: Stress-strain curve for PU foam sample under compression testing. Included: linear elastic region, collapsing region, and densification region [11].

Dynamic mechanical analysis (DMA) in simple shear will support the classification of the spring and damping abilities of foams in the medial/lateral and anterior-post directions during running applications. Nonlinear viscoelasticity describes the stress lag resulting from an input strain. Equation 1 and 2 describes an oscillatory shear input,

$$\gamma = \gamma_0 \sin(\omega * t) \quad (1)$$

$$\tau(t) = \tau(t)_0 \sin(\omega * t - \delta) \quad (2)$$

where ω is frequency and δ is phase lag. The phase lag is a dimensionless value representing the viscoelastic damping of the material.

Equation 3 depicts the shear storage (G') and loss modulus (G'') which corresponds to how much the material stores and dissipates energy, respectively [9].

$$\tau(t) = \gamma_0 G' \sin(\omega t) + \gamma_0 G'' \cos(\omega t) \quad (3)$$

Testing Procedure

An Acumen MTS electrodynamic machine with a 5 kN load cell was used to perform dynamic mechanical analysis. Cylinder foam samples were cut from the midsole to 22.5 mm diameter and 10 mm thickness. Cyclic input strains of 1% to 50% were performed in simple shear at 1 Hz and 5 Hz, simulating the contact times of walking (500 ms) and fast running (100 ms), respectively [12]. The shear testing device can be seen in Figure 3. Force and displacement data was collected at 100 Hz and was analyzed at the 5th cycle to ensure a steady state response [11].

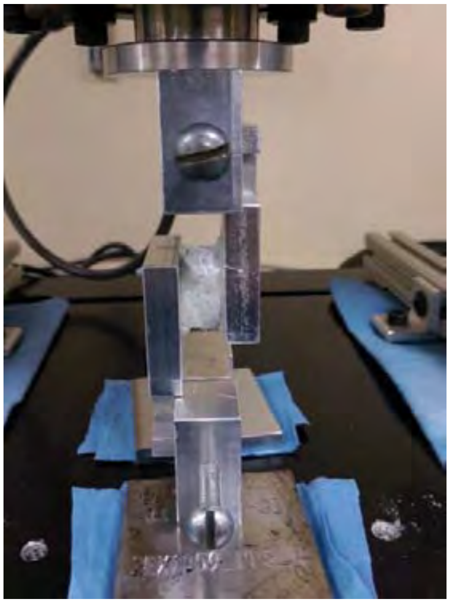

Figure 3: Shear testing device for testing midsole foam cutout.

Results

Experimental

The viscoelastic foam stress response was collected in shear for strains up to 50%. Shear storage (G') and loss (G'') modulus were graphed in Figures 4-7. Both modulus' gradual decreases in the EVA foam, while the E-TPU foam remains unchanged after 5% strain. The storage and loss modulus of the E-TPU material also shows significantly lower values.

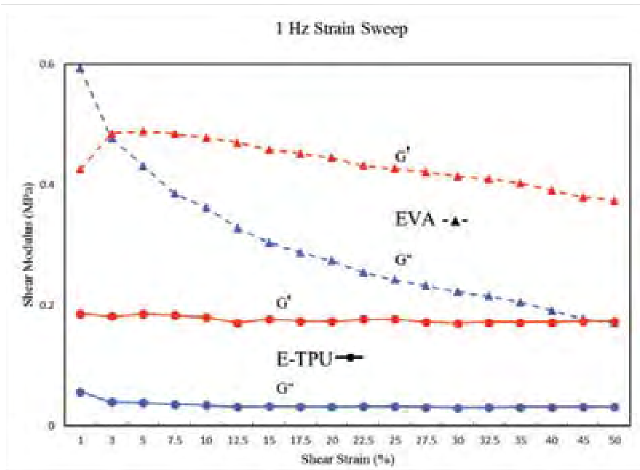

Figure 4: Storage and loss shear modulus of E-TPU and EVA at 50% strain sweep at 1 Hz input.

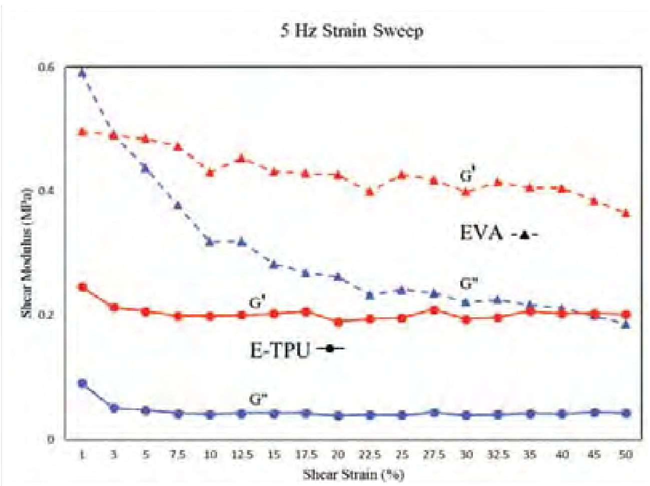

Figure 5: Storage and loss shear modulus of E-TPU and EVA at 50% strain sweep at 1 Hz input.

Lissajous loops for 15%, 25%, 35%, and 45% strain at 1 Hz and 5 Hz can be seen in Figures 6-9. EVA depicts more nonlinear behavior and energy dissipating properties. The 5 hz tests show greater hysteresis than the 1 hz tests for both foams. E-TPU at 35% strain was removed from Fig 7 due to measurement errors. There was a significant increase in energy loss at 50% strain for EVA.

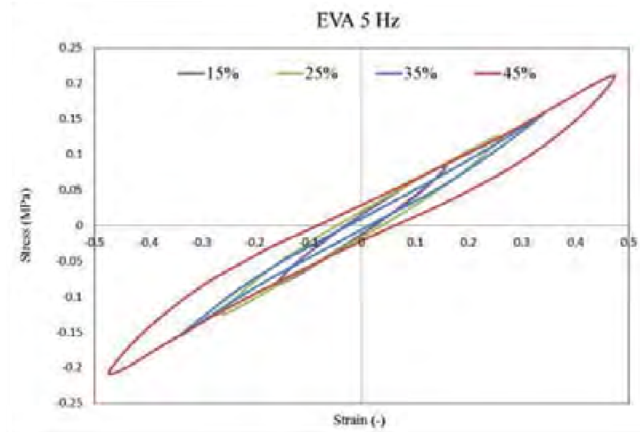

Figure 6: Lissajous loop for EVA at 5 Hz.

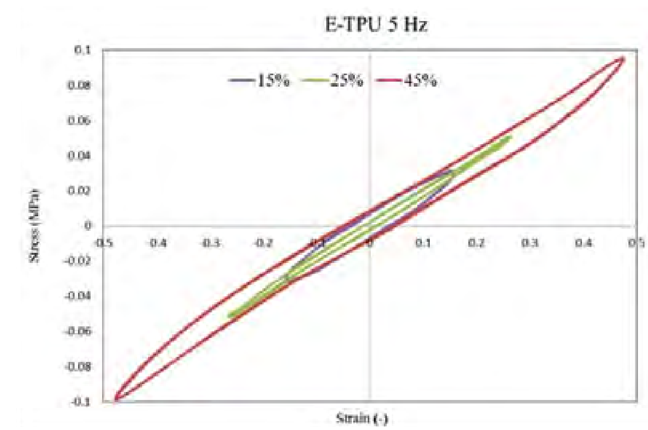

Figure 7: Lissajous loop for E-TPU at 5 Hz.

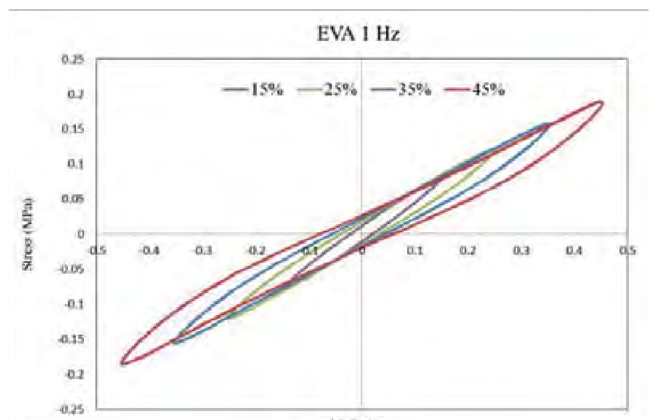

Figure 8: Lissajous loop for EVA at 1 Hz.

Table 1: Coefficients for 2nd order Odgen Hyperfoam model of EVA and E-TPU in simple shear.

Polymer Foam		μ_1	μ_2	α_1	α_2	β_1	β_2
1 Hz	EVA	12.65	12.65	.0409	.0409	0	0
	E-TPU	3.523	3.523	.0538	.0538	0	0
5 Hz	EVA	13.75	13.75	.0400	.0400	0	0
	E-TPU	6.214	6.214	.0315	.0315	0	0

Discussion

EVA depicts more nonlinear behavior due to gradual decreases in the elastic and viscous modulus values. Alternatively, E-TPU shows more responsive behavior as seen in the Lissajous loops (Figs 6-9). The hysteresis characterization at 5 Hz shows EVA having 113% greater energy dissipating properties at 50% strain than E-TPU in simple shear. The hysteresis values of EVA foam support the higher loss modulus when compared to E-TPU at all shear strains. E-TPU foam demonstrated more linear behavior, which provides the athlete with an enhanced foot-shoe "feel", since there is lower energy loss at ground contact. Additionally, the low storage modulus illustrates E-TPU foam's high compressibility providing the runner with greater cushion at equivalent biomechanical impacts.

Conclusions and Further Investigations

Derivation of viscoelastic behavior of polymeric foams found in athletic footwear was performed in simple shear experiments. The curve fitting function in ANSYS determined the 2nd order Ogden model. The energy damping abilities of EVA were greater than E-TPU, indicating a potential kinematic change for the athlete. A verification of the biomechanical analysis of runners wearing EVA vs E-TPU shoes can offer the polymer engineer insight into developing foams for the appropriate sport activity to reduce injury and provide adequate cushioning.

Furthermore, a 3D midsole Finite Element Model can be examined at max lateral stress seen at mid-stance. The dynamic relationship of body dynamics and stress distribution in the midsole is complex. E-TPU compression data can be inputted into multiple experimental tests to accurately represent the combination of stresses experienced during typical gait situations.

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