New Reinforcing Materials for Rubber (Room 1)
Chair: Lewis Tunnicliffe, Birla Carbon

7:45 a.m. Highly Air Impermeable Graphene-Carbon Black Hybrid Nanocomposites for Tire Applications - T R Aswathy, Indian Institute of Technology Kharagpur

The present work aims to provide an extensive study of barrier and mechanical properties that are required for tire applications based on developed binary blend nanocomposites. Graphene nanoplatelets (GNP), in its dispersed form, are capable of developing a tortuous pathway in the rubber matrix, which will retard the passage of gas molecule through the nanocomposites. In this study, composites based on blends of bromobutyl rubber (BIIR) with ENR 25 (epoxidized natural rubber with 25 % epoxidization) and ENR 50 (epoxidized natural rubber with 50 % epoxidization) were prepared, thereafter different levels of carbon black were replaced with GNP to produce hybrid nanocomposites. Barrier and various mechanical properties of both blend based nanocomposites were compared to study the level of exfoliation and reinforcement behavior of GNP. The effect of epoxidation level on the dispersion of GNP has been analyzed with X-ray diffraction and transmission electron microscopy. Morphological studies reveal the formation of nanostructures in BIIR-END blends, and the interaction between the GNP and epoxy groups in BIIR-END nanocomposites was confirmed by BRC and FTIR spectroscopy. The formation of a mixed filler network showed a synergistic effect on the improvement of electrical as well as various mechanical properties. A nanocomposite of BIIR/ENR blend reinforced with GNP can be used in tire applications, because of its enhanced air impermeability and dynamic mechanical properties of the final product.

8:15 a.m. Graphene based Hybrid fillers as New Reinforcing Agents for Tire Industry - Anil Bhowmick, The University of Houston

Rubbers are usually fabricated by adding fillers to meet demands in multi-faceted industrial applications. Reinforcing fillers like Carbon Black and Silica provide excellent mechanical strength and dimensional stability to a rubber vulcanizate. Nevertheless, further enhancement of rubber properties by introduction of novel materials has been an exciting area of research, especially with reference to development of light weight radial tire and tire for electrical vehicles. Graphene is being explored recently. It is a two-dimensional sheet of sp2-hybridized carbon, has exceptionally high specific surface area, and mobility of charge carriers. Due to these unique properties, graphene is considered to be an ideal, nano-sized, multifunctional filler for the above applications. However, despite its high mechanical strength, graphene has not been shown to significantly improve rubber properties, possibly due to its poor dispersibility in a rubber matrix. In the present work, four different graphenic materials- Graphene oxide (GO), Reduced Graphene Oxide (RGO), two type of Graphene nanofillers having variation of surface area (GP1 and GP2)- have been taken for complete evaluation in natural rubber and styrene
butadiene rubber compounds. Dispersion of the fillers in the rubber was carried out by using a proprietary process. Pristine graphene fillers at high loading did not impart significant properties and hence hybrid fillers were used in this study. We have examined four different aspects, i.e. effect of nature and loading (1, 3, 5 and 7 phr) of graphene in a hybrid filler system, keeping the total filler (carbon black (N234) and graphene level) constant at 45 phr, effect of loading of carbon black keeping the graphene level constant at 5 phr, and effect of nature of rubber for a fixed hybrid filler (40phr N234: 5 phr Graphene) system. A reference compound with 45 phr of N234, without graphenic materials, was also prepared.

Graphene nanofillers were found to exhibit superior mechanical and dynamic properties as compared to GO and RGO. Incorporation of GP1 and GP2 in a natural rubber compound had significantly enhanced 300% modulus, tensile strength, tear strength and rebound resilience. The abrasion resistance of these compounds was significantly superior to the GO and RGO based compounds. The enhancement in properties was attributed to a greater degree of exfoliation of graphene nano-platelets and dispersion of carbon black in the rubber matrix as well as their rough surface characteristics. The properties of natural rubber compound containing the graphenic materials were found to reach an optimum at a loading of 5 phr graphenic material and 40 phr of carbon black. A decline in tear strength was observed with increasing loading of graphenes. At higher loading of carbon black (60 phr), the effect of graphene is not always significant. The enhancement in rubber properties was also observed in styrene butadiene rubber (SBR) based formulation containing 40 phr of N234 and 5 phr of graphene nanofiller. The extent of improvement in SBR based compound was found to be greater as compared to the NR based formulation.

8:45 a.m. Joint Hybridization of Secondary Fillers and Secondary Polymers Towards Improved Silica-Reinforced NR Tire Tread Compounds - Wisut Kaewsakul, University of Twente

To improve the properties of silica truck tire tread compounds, especially abrasion resistance, the effect of vinyl-contents in Butadiene Rubber (BR) or Solution Styrene Butadiene Rubber (SSBR) as secondary polymers in silica-filled Natural Rubber (NR) compounds at a ratio of 80/20 phr, is investigated in the first part. By increasing the vinyl-content in BR in combination with NR, a better Payne effect, 300% modulus, reinforcement index, tan delta at -20°C and 0°C are obtained, whereas tensile strength, elongation at break and DIN abrasion resistance index decrease with increasing vinyl-content. Increasing vinyl-contents in SSBR show improvements in Payne effect, 300% modulus, tan delta at -20°C and 0°C and a little in DIN abrasion resistance index. The combination of secondary filler and polymer in silica-filled NR are covered in the second part of the present study. Silica/Carbon Black (CB)-filled NR/BR and NR/SSBR, resp. silica/OrganoClay (OC)-filled NR/BR and NR/SSBR show positive effects on the scorch time, optimum cure time, with slightly changed Payne effect, tensile properties, tan delta at -20°C and 0°C, and DIN abrasion resistance as compared to the compound with CB N134. The use of OC shows enhancement in Payne effect and tan delta at 600°C, indicative of a reduced filler-filler network and consequently lower rolling resistance of the tire tread compound compared to the compound without OC.

9:15 a.m. Break & Table Top Exhibits

9:30 a.m. Micro- Vs. Macro- Dispersion: Payne Effect as Indirect Micro-Dispersion Measurement for Silica-Reinforced Elastomer Compounds - A. Kharel, University of Twente

The process of mixing silica into an elastomer determines the interaction between the different components and significantly influences rheological properties, shaping processes and final mechanical properties. Mechanical breakdown of silica clusters as well as a chemical reaction between silica and silane coupling agent have to occur
simultaneously during mixing. The breakdown of silica clusters generates a distribution of filler particle sizes ranging from light microscopically visible macro- to sub-micron dispersion. It is the latter which has the most significant influence on the mechanical properties because the sub-micron clusters are the real reinforcing species. It is a challenge to maintain a consistent level of micro-dispersion between every mixed batch. Can the Payne effect be employed as an indirect but reliable indicator for micro-dispersion and inter-particle interaction? The paper will review recent advances in our research on answering this fundamental question.

10:00 a.m. Nanodiamond as a New Reinforcing Material for Natural Rubber - Seiichi Kawahara, Nagaoka University of Technology

The distribution of nanodiamond inside a nanomatrix, which is related to the mechanical and viscoelastic properties, is investigated for a natural rubber-nanodiamond composite. The composite is prepared by reacting nanodiamond with deproteinized natural rubber (NR-ND) in the presence of a tert-butylhydroperoxide (TBHPO) / tetraethylenepentamine (TEPA) radical initiator at 30 °C in the latex stage and subsequent drying. The morphology of the composite is observed by 3D transmission electron microscopy (TEM). NR-ND prepared with an initiator exhibits a nanomatrix structure, whereas NR-ND prepared without an initiator displays an island matrix structure. The nanomatrix is densely loaded with 15 nm or smaller-sized nanodiamond. Both the mechanical and viscoelastic properties of NR-ND depend upon the morphology. The stress at break and plateau modulus are 12 MPa and 1.19 × 106 Pa when NR-ND is prepared with a TBHPO/TEPA initiator and contains 25 w/w% nanodiamond, which are four and eight times higher than those of DPNR, respectively.

Sustainable Developments in the Tire Industry (Room 2)
Co-Chairs: Lena Nguyen, Dow Chemical and Amy Landis, Colorado School of Mines

7:45 a.m. Latest Trends in Tyre Retreading Technology - Sabari Nadha Prasad, Eastern Treads Ltd.

This Presentation covers the latest technology for various tyre retreading processes like Pre-Cured Tread Rubber, Hot Rubber, Ring Tread, Orbi Tread, Flex Cure, Vaculug etc. and includes an overview of Tread Design criteria and its impact on Performance parameters in tyre service life. We will discuss he latest trends in Tyre Retread Curing in Electric Chamber and Thermocouple studies to optimise tyre endurance. We will cover the latest Trends in Rubber Compounding for manufacture of Tyre Retreading materials like Cold Rubber, Hot Rubber, Bonding Gum, Cushion Gum, Vulcanising Cement, Tyre Patches, Envelopes etc. Finally, we present an attempt on tyre wear mechanism and correlation of Viscoelastic Properties on tyre endurance with a vision for developing a one Million Mile Tyre with multiple Retreading.

8:15 a.m. The Use of Biobased Estolides in Tire Processing - Mark Miller, Biosynthetic Technologies

Green initiatives are everywhere. Bio-fuels, wind energy, renewable fibers are just a few of the environmental initiatives that have recently made headlines. Meanwhile some of the greatest innovations have been in the development and utilization of high performance, environmentally acceptable process oils. This paper/presentation focuses on the innovations, features, benefits, strengths and limitation of the different types of green processing oils. It will review the test work that has been done replacing Naphthenic petroleum oils with biobased Estolide and 50-50 combinations. The paper will also review
the results of biobased estolides in a variety of elastomers as compared to petroleum oils and other environmentally preferable products. The different definitions of environmental acceptability and why that is important will be explored. The regulatory driving forces will be identified as well as the requirements for each.

8:45 a.m. Technical Approaches for the Continuous Devulcanization of ELT Material - **Mathias Zabel**, KraussMaffei Extrusion GmbH

The comprehensive treatment of End of Life Tires (ELT) is pressing. The previous disposal options such as landfill, incineration or dumping are unpopular. Other approaches must be found to meet the never-ending increase of ELT. Especially for the public image of the tire industry: The tire, a durable mixture of materials, non-biodegradable and ecologically difficult in the treatment, has a bad reputation.

As of today, 2.5 billion tires are produced each year, although their disposal is regulated inconsistently. In order to master the sheer quantity of ELT, the only alternative is to introduce the ELT upcycling to the Circular Economy. Already local sustainability regulations at the legislative level start to require 5% of recycled material in new tires.

It takes a lot of effort to prepare the sophisticated waste source for the purpose of sustainable environmental protection. Apart from compliance with specified process temperature, only the sulphur bridges shall be affected. At the same time, the polymer structure must be maintained. Otherwise, significant losses in the mechanical properties and product quality occur on re-introduction to the value chain.

Technical approaches include the use of single-screw and twin-screw extruders. Depending on the individual solution chemical additives may also be used to prepare the polymer matrix for re-vulcanization. Also water may be added to the rubber processing to stop energy dissipation. There has been found a general rule: The more mechanical energy is introduced, the less chemical additives are needed. Thus, complex solutions consisting of several twin-screw extruders don’t need any chemical additives and may provide a more environmentally friendly solution. Also, the local application of cooling in the process is one way to cope with the associated energy dissipation.

9:15 a.m. Break & Table Top Exhibits

9:30 a.m. New Processes for a Modification of Ground Rubber Particles Produced from Spent Tires and their Anticipated Impact on Rubber Recycling - **Georg Bohm**, Appia LLC

Currently encountered rubber recycling problems will be redefined and discussed from a materials science perspective. This will be followed by a discussion of recent results with new processes under development that can convert ground rubber particles of spent tires, inexpensive fillers of marginal performance, into higher value raw materials for use in new tires and other applications.

10:00 a.m. Sustainable Rubbers from Renewable Biomass - **Anil Bhowmick**, The University of Houston

Sustainable materials are defined as materials that can be produced without depletion of non-renewable resources and without disturbing the equilibrium between the environment and key natural resource systems. Rubber is one of the most versatile materials having myriad of applications. However, many rubbers suffer from sustainability issues.

With a quest for developing sustainable rubbers, the rubber industry has accepted a great challenge of utilizing renewable resources to replace petrochemical-based monomers. Biobased feedstocks are used increasingly in the production of rubbers. Natural rubbers from Hevea Brasiliensis, Parthenium Argentatum etc. have been widely utilized to design rubber products for over hundred years. On the contrary, monomers from terpenes,
vegetable oils, lignin etc. have attracted interest only recently. Terpenes, which are readily available in large scale, have a great potential to substitute currently used petrochemicals. We have synthesized different rubbers from β-myrcene, the acyclic mono terpene, via a greener route like conventional emulsion polymerization. The polymyrcene synthesised following two different optimized set of reaction conditions showed high molecular weight, mixed microstructures and interesting physical properties. In order to impart polarity into polymyrcene, improve interactions with various functional fillers, and synthesize smart and high performance rubbers, modification and functionalization of bio-based rubbers have been carried out. Incorporation of polar groups promotes the filler (carbon black and silica) dispersion in rubber compounding. The rubber vulcanizate exhibits good wet skid resistance as well as lower rolling loss when compared with a standard tire tread compound, making it an appealing material for automotive sectors. The materials display similarity to conventional petro derived styrene butadiene rubber (SBR). Self-healing elastomer has been also prepared by this green technique. In the context of sustainability, we feel that these kinds of terpene-based rubber could be an ancillary material to replace the petroleum based products in various applications.

10:30 a.m. Optimization of Processing and Performance of Truck Tread Compounds Utilizing Organic and Inorganic Processing Aids - Miles Dearth, Spherix Products

A multi-factor, general factorial design of experiments is performed to investigate the use of optimized combinations of conventional organic process aid, together with sustainable ceramic microspheres in a 2-pass carbon black reinforced natural rubber compound. The factors selected for experiments are surface functionality of microspheres, phr levels of spheres and type of organic process aid. The measured dependent variables include: a) dispersion (ASTM D7723), b) RPA (ASTM D6204), c) Payne Effect (ASTM D8059), d) physical properties (ASTM D412); e) Pendulum Rebound (ASTM D7121), f) DMA temperature sweep, g) Din Abrasion; h) Spider molding and i) Garvey Die Extrusion.

11:00 a.m. KEYNOTE ADDRESS: Ali Dhinojawala, The University of Akron College of Polymer Science & Polymer Engineering

12:00 p.m. Lunch Break & Table Top Exhibits

New Reinforcing Materials for Rubber (Room 1)
Chair: Lewis Tunnicliffe, Birla Carbon

1:15 p.m. New Insights in the CNT-Rubber Structure for a Rational Development of Advanced Materials - Juan Lopez Valentin, Institute of Polymer Science and Technology ICP-CSIC

Carbon nanotubes (CNT) have attracted a huge interest in both academia and industry because their exceptional mechanical, electrical and thermal properties. In addition, their large aspect ratio, low density and high flexibility make CNT a unique nano-filler to develop advanced rubber materials. Although CNT-rubber nano-composites show enhanced characteristics in comparison to their micro-composite counterparts (e.g. based on carbon black or silica-silane systems), they have not been able to reach the expected properties.

In this work, a systematic characterization of CNT-rubber structure has been performed by using a combination of experimental techniques (including advanced 1H time-domain NMR methods) and the last developed analysis procedures (including stress and strain amplification factors) in order to improve the understanding about the mechanical and
viscoelastic properties of these nano-composites. Combination of uniaxial tensile properties, equilibrium swelling experiments and double-quantum (DQ) NMR experiments has revealed a strong contrast in the constrain density at the CNT interface where the molecular weight between interactions (including cross-links and entanglements) is shorter than in the bulk. Despite the enhanced filler-rubber interaction (in comparison with traditional rubber composites), the main reinforcing factor that govern the mechanical properties of these nano-composites is the filler network (with a percolation threshold at very low CNT volume fraction).

According the new insights in the CNT-rubber structure, these promising materials could have some limitations to be applied in high-performance tire tread compounds (mainly related to the rolling resistance and fuel consumption) because of the difficulty of dispersion of CNT in rubber matrices (high filler networking), the strong influence of CNT in the vulcanization process (low cross-link density and high network defects) and the nature of filler-rubber interactions (high energy dissipation associated to the rupture of filler-rubber interactions at high strain amplitudes). To overcome these issues, the CNT have been surface-modified with oxygen-bearing groups and sulfur, in order to achieve i) better dispersion of CNT in the elastomeric matrices, ii) formation of covalent bonds between rubber chains and the CNT surface and iii) reduction of network defects.

1:45 p.m. High Efficient Anisotropic Fillers for Advanced Properties and Light Weight - Ulrich Giese, German Institute of Rubber Technology e.V. (DIK)

From technical and from sustainability aspects modern rubber compounds have to fulfill a lot of properties on very high levels. Low permeation rates for gases and liquids, high strength and low density (light weight) are some of the most interesting demands from technical application of rubber compounds. Such high sophisticated properties can be reached using anisotropic fillers like layered silicates, nano-fibrillated cellulose (NFC), carbo nano tubes (CNT), carbo nanohorns (CNH) or graphene platelets. The high potential of such filler materials can be used only in combination with optimized mixing strategies for high dispersion. Outstanding results in dispersion of the special fillers could be obtained using a promising special latex mixing technology. Raw materials are original latex or secondary latex in the case of special rubbers, available normally as solid rubber only, because of solvent polymerization processes. NFC-composites with low density at high mechanical strength and hardness could be prepared. By means of a planetary mixer special soft electrode materials were prepared using silicon in combination with electric conductive fillers at extremely low perculation levels.

2:15 p.m. Utilization of Enzyme to Bioprocess Soybean Hull into Nanoparticles for Use as Reinforcing Fillers in Rubber - Vamsi Bhadriraju, The University of Akron

The unrenewable petrochemical origin of carbon black, a common filler in rubber composite processing, has motivated further research into finding alternatives for reinforcing fillers. Past ventures into creating filler alternatives have involved varying ratios of rubber blends, filler concentrations, and additives in the compounding formula. In recent years, micro- and nanocellulose have emerged as versatile and environmentally-friendly alternatives for petroleum-derived fillers for composite applications. Our research lab specializes in producing fungal enzymes, specifically carbohydrases. Soybean hull was
used for enzyme hydrolysis because of low lignin and moderately high cellulose content. After batch fermenting a selected fungus on soybean hull, the harvested enzyme cocktail is used in the hydrolysis of soybean hull. This enzyme hydrolysis completely breaks down the non-cellulosic carbohydrates present in the biomass. After hydrolysis, the solubilized components are removed and the resulting solids are homogenized. The suspensions of soy-nanoparticles collected are then evaluated as reinforcing fillers for rubber compounding. Observations, results, and discussion for further development will be presented.

2:45 p.m. Preparation and Properties of Natural Rubber with Nanodiamond Nanomatrix Structure - Seiichi Kawahara, Nagaoka University of Technology

Effects of nanodiamond on the mechanical properties of natural rubber were investigated by forming nanomatrix structure in the rubber. Natural rubber with the nanodiamond nanomatrix structure was prepared by chemical reaction of the rubber particles with nanodiamond in latex stage followed by drying. Dynamic mechanical analysis, differential scanning calorimetry, transmission electron microscopy were carried out for natural rubber with the nanodiamond nanomatrix structure. Energetic elasticity in conjunction with the entropic elasticity were investigated in relation to bound rubber between natural rubber and nanodiamond. A significant increase in complex modulus for natural rubber with nanodiamond nanomatrix structure was attributed to the complex modulus of the bound rubbers.

3:15 p.m. Break & Table Top Exhibits

3:30 p.m. Modification of Vulcanized Natural Rubber-Bacterial Cellulose (NRBC) Composites via Thermo-Responsive and pH Responsive Polymers - Sirilak Phomrak, The University of Akron

In a previous study, we demonstrated vulcanized natural rubber (NR) composites reinforced with bacterial cellulose (BC) had been successfully prepared via a latex aqueous microdispersion process and vulcanized with sulphur system. Vulcanized NRBC composites shown layered structure or laminated structure. For mechanical properties, their Young’s modulus and tensile strength were enhanced with the increase of BC content, while elongation at break decreased. In this study, we focus on functionalizing the NRBC to exhibit thermo-responsive and/or pH responsive properties using relevant polymers (e.g., poly(N-isopropylacrylamide) (pNIPAAm), poly(vinyl methyl ether) (PVME), and poly(sulfonic acid) (PSS)). The polymer was blended with a silane coupling agent, e.g. 3-aminopropyltriethoxysilane (APTES), and the coated on NRBC and subsequently annealed thermally. The modification was achieved for NRBC, especially for NRBC with a higher BC content, due to the hydroxyl groups in BC. BC contents in NR matrix, APTES/pNIPAAm ratio and APTES/pNIPAAm concentration were optimized to fabricate the responsive NRBC composites that are expected to have potential applications in medical, membrane separation and waste oil recovery.

4:00 p.m. Novel Crosslinking Strategies Toward Strengthened and Malleable Rubbers - Baochun Guo, South China University of Technology

Traditionally, strengthening of rubber mainly depends on the incorporation of nanoparticles. On the other hand, the recycling of crosslinked rubbers has been limited to low-end and polluting applications, such as reclaimed compound by desulfurization, powdered rubber as filler and low-grade oils by pyrolysis. Therefore, it is highly desirable to seek a “Cradle to Cradle” strategy to initiate a closed recycling loop at the end-of-life of rubbers without compromising performance. This talk summarizes our work on the
development of strengthened and reprocessable rubbers via crosslinking design. On the one hand, two kinds of crosslinks with variable bond strength are introduced into the rubber network. The weaker crosslinks act as sacrificial bonds under external loading, i.e., they can preferentially break while the crosslinks with higher bond energy maintain the integrity and good resilience. The consistent fracture of the sacrificial bonds lead to the dissipation of numerous mechanical energy and promote the orientation of rubber chains, leading to significantly improved strength and fracture toughness. The achieved mechanical properties are comparable to those of the filled rubbers. We further demonstrate that not only weak bonds, but also short chains or deformable domains can act as sacrificial units through similar mechanisms. On the other hand, we designed a number of rubbers crosslinked by dynamic covalent bonds. Because of the exchangeable nature of the crosslinks, the rubbers exhibit promising reprocessability with high recovery of performance. We have developed a series of reinforcing strategies for these malleable rubbers, including the introduction of interfacial dynamic covalent crosslinking, the solid-state stretching of rubber composites with high aspect-ratio fillers, and the introduction of sacrificial bonds. These methods provide new solutions for the preparation of rubbers with the combination of reprocessability and high mechanical performance.

4:30 p.m. Reinforcement of Rubber by Lignin Coated Nanocellulose Fibrils - Lewis Tunnicliffe, Birla Carbon

Lignin coated nanocellulose fibrils (LCNF) have potential as a biomass-derived, functional reinforcing agent for rubber goods and tires. This paper explores the reinforcing effects of LCNF in natural rubber compounds as a synergistic filler alongside conventional carbon blacks. The ability to increase sustainable raw material content in rubber compounds while also maintaining or improving critical compound properties such as hysteresis and tear resistance is detailed. The anisotropic nature of the LCNF is characterized in terms of micro-dispersion state and alignment under shear of fibrils and also in subsequent mechanical properties.

3D Printing with Elastomers (Room 2)
Chair: Chris Robertson, Endurica, LLC

1:15 p.m. 3D Printing of Silicone Elastomers Using Freeform Reversible Embedding (FRE) - Adam W. Feinberg, Carnegie Mellon University

Polydimethylsiloxane (PDMS) is an elastomer widely used in industry due to its low elastic modulus, high elongation to failure, optical transparency, and excellent thermal and chemical resistance. These properties make PDMS desirable for the fabrication of custom-maid medical devices, such as orthopedic insoles and respirator masks, and the generation of tissue phantoms for surgical planning. PDMS is typically formed via casting and molding techniques, but these approaches are limited in their ability to produce complex, patient-specific geometries in three dimensions. To address this issue, our lab previously developed an additive manufacturing technique, freeform reversible embedding (FRE), that enables 3D printing of soft materials into complex architectures via entrapment within a soft, viscoelastic support matrix. Even with the support, however, it is difficult to print elastomeric polymers like PDMS due to the liquid state of the prepolymer. Furthermore, material deformation during extrusion in such embedded 3D printing systems is not well understood, which is critical for optimizing machine pathing. Here, we report the modification of PDMS rheology to enhance printability and subsequent investigation into material deformation by analyzing the morphology of extruded filaments. Finally, machine pathing is optimized to produce constructs with high fidelity.
3D and 4D Printing of Elastomeric and Rubber Materials - *Rigoberto Advincula*, Case Western Reserve University

The use of 3D printing to create prototypes and devices from elastomeric and polymeric materials has appended the design functionality for new materials including uses in biomedical devices enabling rapid development While 3D printed polymers can be further classified into thermoplastics, thermosets, and elastomers based on their thermo-mechanical properties. The processability and functionality of rubbers and elastomers make it a challenge to employ 3D printing methods for additive manufacturing. The transition to a final phase or cross-linked structure results in new properties in combination with the processing method. This is more evident with the choices of 3D printing methodologies (FDM, SLA, SLS, VSP) which can make use of blended or formulated compositions. We have demonstrated the 3D printing of biomedical grade thermoplastic polyurethanes (TPU), silicones, and rubberized epoxies. However, 4D printing allows the design of new materials and applications based on integrating the chemistry of conversion with the printing mode. In this talk, we demonstrate the fabrication of concept objects and elastomeric actuators based on the use of biomedical grade TPU melts and extruded viscous solutions. The result is an extrudable precursor and nanocomposite elastomers which can be printed via viscous extrusion printing (VEP) or VSP and then converted to an elastomeric actuating materials with very high cyclic compressibility. Other work based on the use of SLA, SLS, FDM, towards high strength silicones and nanocomposite materials will be discussed.

2:15 p.m. Breakthroughs in 3D printing - *Matthew White*, American Additive Manufacturing

What is 3D Printing/Additive Manufacturing? This talk will discuss the differences between additive and subtractive technology and economic implications of additive manufacturing. Through case studies, application videos and industry insight, we examine the key industrial verticals where AM is having a significant impact; process, software and material breakthroughs; the use of elastomers in 3D printing; the skills gap and resources to get involved & areas of opportunity.

2:45 p.m. Additive Manufacturing of Elastomers (AME, Rubber 3D) - *Lion Sundermann*, German Institute of Rubber Technology e.V. (DIK)

Additive manufacturing of thermoplastics or metals is a well approved process for obtaining rapidly precise and individual technical components. Except for crosslinked silicone rubber or thermoplastic elastomers, there is no way of manufacturing elastomers. Based on the development of the Additive Manufacturing of Elastomers (AME) – process, the material group of elastomers may get first access to the process field of 3D-printing. The printing and crosslinking of the rubber is separated in two steps: First the printing is realized by extrusion of the rubber by using a small extruder, working according to a derived Fused-filament-fabrication (FFF) principle. In the second step the component is vulcanized in a high pressure hot-air autoclave. Fused-filament-fabrication (FFF) means, that thermoplastic filaments are molten and extruded through a nozzle and placed in a defined geometric manner. Due to the plastic flow behavior of non-crosslinked rubber materials, the FFF has to be adapted to keep the extruded material in shape. Therefore a thermoplastic mold is needed to keep the geometry and position of the extruded rubber. In this way one layer of thermoplastic and one layer of rubber are printed alternatingly until the component is finished. The extrusion temperature of the rubber mixture is typically between 80 and 100 °C and of the thermoplastic between 230-270 °C. The in this way additive manufactured binary component is placed in the autoclave to obtain the elastomer after vulcanization under hot air and high pressure atmosphere. The geometric stability of
the mold is up to 190 °C, so that the shape of rubber material is retained. The thermoplastic mold can be removed from the elastomer and recycled afterwards. The high viscosity of rubber during processing compared to conventional thermoplastics and the unstable shape after extrusion is challenging in the development of the AME.

3:15 p.m. Break & Table Top Exhibits

3:30 p.m. Silicone Elastomers for Sustainable Additive Manufacturing - Remi Thiria, Elkem Silicones

Silicone elastomers are widely used in healthcare and biomedical applications as a result of their chemical inertness, hypo-allergenicity and high performance physical properties (flexibility and durability, electrical resistance, optical properties…). They are also materials of choice due to their stability across a wide range of environmental conditions (such as body fluids, skin atraumatic for wound care, inert with sterilization conditions). The demand about individualized medical devices through 3D printing incorporating elastomeric materials is growing fast and silicone elastomers are strongly targeted. Indeed, they enable to get high mechanical elastomeric performances without loss of properties during ageing giving high sustainability for functional 3D printed medical devices. Despite the progresses of AM liquid extrusion processes (Liquid Deposition Modeling) with silicone elastomers, there is always the issue for energy consumption with low production rate when compared to injection molding processes and the need of a support material (overcoming overhangs) and increasing the amount of wastes after processing. During this presentation we will show how we can achieve 3D printing of high viscous silicones such as Liquid Silicone Rubbers in a sustainable approach without dispensing high curing energy and reducing support wastes. As a provider of medical and drug delivery grade silicone elastomers, Elkem Silicones is uniquely positioned to work with medical device manufacturers and fabricators on AM solutions. We will also implement the 3D silicones technology approach with some applications such as for soft robotics, sealing and or functional anatomic models.

4:00 p.m. Predicting Durability of 3D Printed Elastomeric Lattice Structures - Chris Robertson, Endurica, LLC

ABSTRACT IN PROCESS

Wednesday, April 29th

Fracture Mechanics of Elastomers, Networks and Gels (Room 1)
Chair: Will V. Mars, Endurica, LLC

7:45 a.m. Analysis of Domain Break in the Elongation of TPE using CGMD Simulations - Hiroshi Morita, AIST

The elongation process of thermoplastic elastomer (TPE) is simulated using coarse-grained molecular dynamics (CGMD) simulation. In TPE, bridge and loop chains are formed. In the elongation process, bridge chains are elongated, and some hard domains break. In this study, we focused on the coalescences and breaks of domains with changing the deformation rate from the analysis of each polymer chain in CGMD simulations. Along the deformation rate, the relaxation of polymer chains is changed and the structure of broken domains are also influenced. The detail mechanism of domain break will be presented.
8:15 a.m. Numerical Leak Prediction of Elastomeric Seals - Travis Hohenberger, Queen Mary University of London

Elastomeric seals are used for pressure isolation in various applications. Design criteria for some seals such as O-rings are well-established, allowing simple determination of a working design. However, such criteria are empirically derived and not generally applicable to other geometries. This presents a challenge with complex seals where closed form solutions for failure prediction do not exist. Such failures are due to fracture, elastic leak, or a combination of both. Literature on the fracture mechanics of elastomers is abundant, but leak prediction has received less attention. It is even unclear which leak criteria to adopt for numerical simulations, but they typically fall into one of two categories: leakage when contact pressure at the sealing interface is zero or leakage when contact pressure equals applied fluid pressure. To compare these two criteria, finite-element (FE) simulations of bonded plane strain rectangular and axisymmetric face seals have been conducted. The effect of friction has been included in these models, and the simulations suggest that the coefficient of friction is a critical parameter for maximising sealing capability. Prediction of seal leakage is also found to strongly depend on mesh size, pressure penetration criteria, and pressure integration scheme.

8:45 a.m. Polymer Tack and Interfacial Crack Mechanics - Xiaorong Wang, Institute for Advanced Study, Tongji University, Shanghai

We have studied the tackiness of polyisoprene melts by pulling out a cylindrical probe from the polymer surface over a range of separation speeds. The probes were varied with materials and surface roughness. The polymers were either linear or star-branched, with the molecular weights of the former ranging from 80 to 500 kg/mol and of the latter from 400 to 4000 kg/mol. We find that when the pulling speed (Vs) is greater than a critical speed (Vc), the maximum tack force (Fmax) can be generally described by the following scaling relationships: Fmax ~ Vs^{1/3} and Fmax ~ tmax^{-1/2}, where tmax is the time when the maximum force is reached. This scaling behavior of the tackiness appears to be universal and is to a large extent independent of the polymer architectures and probe surfaces. We show that these universal scaling relations are related to the physics where the tack is controlled by the crack propagation along the interface. The micro-cavitation or fibrillation in the separation of rubber-probe interface seems largely irrelevant. A summary of our recent research activities at Tongji on this subject will be presented.

9:15 a.m. Break & Table Top Exhibits

9:30 a.m. Intrinsic Strength and Tearing Behavior of Tread Rubber Compounds - Nihat A. Isitman, Goodyear Tire & Rubber Company

While a number of studies discuss the ultimate tearing behavior of unfilled rubber compositions and how it is influenced by basic formulation variables, for instance, the choice of elastomers, crosslink density or the nature of crosslinks, there is limited understanding of how those ingredients influence threshold energy (T0), crack propagation rate and critical tearing energy (Tc) for high loading levels of silica in tire tread compounds. This research investigates the effects of basic formulation variables in filled model tread rubber compounds on general tearing behavior using a variety of techniques such as intrinsic strength analysis to determine T0, cut growth analysis to establish crack growth rate as a function of tearing energy, and planar tension (pure shear) tear testing to obtain Tc. The strain and temperature dependent viscoelastic properties will be discussed considering that the tearing behavior at the crack tip zone is influenced by dissipation characteristics. The talk will elaborate tearing behavior of model rubber compounds in relation to polymer blend composition, crosslink density and silica loading.
10:00 a.m. Infinite Life Design Principles for Rubber Structures - **William Mars**, Endurica LLC

Because of its simplicity, the intrinsic strength has great utility as a design rule for rubber product developers. By keeping tearing energy at all times below the intrinsic strength, a designer can assure infinite life with minimum effort. Two examples are considered here: a grommet sizing application, and a tire belt compounding application. In each example, simulation is used to compute the fraction of loading reserve relative to the intrinsic strength.

**Advances in Polymer Blends (Room 2)**
Co-Chairs: **Dominica Wong** and **Malikh Al-Afyouni**, Eastman Chemical Company

7:45 a.m. Characterization of Recycled Polymer Compound by Thermal Analysis - **Yanxi Zhang**, Netzsch Instruments

Thermal Analysis is a powerful method to understand properties of neat polymers and their compounds. DSC determines thermal transitions like glass transition, melting or crystallization. TGA measures humidity and filler content as well as thermal decomposition. DMA measures viscoelastic mechanical properties and TMA measures coefficient of thermal expansion and thermal transitions as well. Every individual method delivers a certain piece of information to distinguish material properties. When combining these thermal methods a more complete picture of polymer compound can be discovered. As virgin polymer compound is more expensive than a recycled material, molders want to evaluate the suitability of alternative recycled compound. Can a recycled compound be used to replace virgin polymer compound? Thermal analysis techniques, such as DSC, TGA, TMA and DMA can answer this question. In this paper TGA, DMA and DSC with “Identify”, a database search software, are used to characterize recycled polymer compounds, PA6-GF30, for pre-selection, which is used to manufacture injection-molded car part.

8:15 a.m. Influence of Electron Beam Irradiation on the Thermomechanical Properties of Styrene-Ethylene-Butylene-Styrene (SEBS)/ Thermoplastic Polyurethane (TPU) Blends - **M G Anagha**, Indian Institute of Technology, Kharagpur, India

Effect of electron beam radiation curing in blends of thermoplastic elastomers were explored in two systems based on SEBS/TPU and SEBS-g-MA/TPU. A non-compatibilized 60/40 blend of SEBS and TPU, and an in-situ compatibilized 60/40 blend of SEBS-g-MA and TPU were irradiated by varying radiation dose from 0, 10, 25, 50 and 100kGy. In SEBS/TPU blends degradation was more pronounced than crosslinking as observed from the deterioration in tensile strength. While in maleated SEBS/TPU blends, crosslinking takes place and the tensile properties improved upon radiation, with highest strength at a radiation dose of 25kGy. Crosslink density calculations were made in order to assess the equilibrium swelling. The morphology of the blends was pursued from Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Changes in storage and loss moduli, complex viscosity and tan delta with respect to frequency upon irradiation were monitored from a parallel plate rheometer. Thermal properties of the blends were deduced from Thermogravimetric Analysis (TGA) and Dynamic mechanical Analysis (DMA). X-Ray diffraction method revealed the changes in diffraction pattern in the blends subjected to EB radiation.
8:45 a.m.  Design Strategy for Self-Healing Epoxy Coatings - Ica Manas-Zloczower, Case Western Reserve University

Extrinsic self-healing materials rely on a secondary phase to acquire the self-healing functionality. Understanding the impacts of the secondary phase on healing performance and matrix properties is important for rational system design. In this work, self-healing epoxy-TPU prepolymer coating systems were prepared by blending a bio-based epoxy diglycidyl ether of diphenolate esters (DGEDP) with a series of different molecular weight thermoplastic polyurethane (TPU) prepolymers. Such systems exhibit polymerization induced phase separation morphology that controls the coatings mechanical and healing properties. Structure-property analysis indicates that the degree of phase separation is controlled by tuning the TPU prepolymer molecular weight. Increasing the TPU prepolymer molecular weight results in a highly phase separated morphology that is preferable for mechanical performances but undesirable for healing functionality. Low molecular weight TPU prepolymers tend to phase mix with the epoxy matrix during curing, resulting in the formation of a flexible epoxy network that benefits TPU flow while decreasing Tg and mechanical properties. This work describes a rational strategy to develop self-healing coatings with controlled morphology to extend their functions and tailor their properties for specific applications.

9:15 a.m.  Break & Table Top Exhibits

9:30 a.m.  Combining Polyethylene and Polypropylene with Multiblock Polymers - James M. Eagan, The University of Akron

Polyethylene and polypropylene are the two most widely used plastics worldwide. The two plastics do not form tough blends however due to phase separation and poor interfacial strength. Novel multiblock copolymers enabled by advances in catalysis and polymer synthesis were used as compatibilizers in iPP/HDPE mixtures and convert brittle materials into mechanically tough blends.

10:30 a.m.  Charles Goodyear Medal Address - Dr. Nissim Calderon, Goodyear Tire & Rubber Company

11:30 a.m.  Science & Technology Awards Banquet

Science & Technology Awards Symposium
Chair: Dr. Maria D. Ellul, ExxonMobil Chemical Co. (Retired)

2:00 p.m.  Melvin Mooney Award for Distinguished Technology - Dr. Kenneth Gillen, Sandia National Laboratories

2:30 p.m.  Sparks-Thomas Award - Dr. David Simmons, University of South Florida

3:00 p.m.  George Stafford Whitby Award for Distinguished Teaching and Research - Dr. Chrys Wesdemiotis, The University of Akron

3:30 p.m.  Break & Table Top Exhibits

3:45 p.m.  Chemistry of Thermoplastic Elastomers Award - Dr. Lewis Fetters, Cornell University
Flow and Aging of Silicone Rubber for Fuel Cell Sealing Applications - Anita Luong, University of Michigan

In a polymer electrolyte membrane fuel cell, seal failure can lead to loss of function, inefficiency, or safety concerns. Commercialization requires the seals to remain robust throughout the life of the fuel cell stack. Therefore, it is advantageous to use application-specific accelerated test protocols complemented by validated material-level degradation models to assess seal robustness and durability. This work studied the degradation of silicone seal materials exposed to heat and fuel cell-relevant environments while under compression. Mechanical behavior was studied using compression and dynamic mechanical analysis experiments. Aging temperatures ranged from 80 to 150°C. Irreversible and reversible changes in the silicone were measured, including stiffening, permanent set, stress relaxation, and recovery. Master curves were generated using time-temperature superposition to determine the kinetics of flow and aging in the seal material. Time at temperature was found to have the strongest effect on stiffening, for which the activation energy was found to be 102 ± 16 kJ/mol. This data is being used to inform the specification of efficient and representative accelerated product validation test protocols and to develop a constitutive material model which can be used in finite element analysis to predict seal performance over time.

The Synthesis of Functionalised Solution Styrene-Butadiene Copolymers Exploiting Myrcene and the “Fire and Forget” Approach - Lian R. Hutchings, Durham University

Solution styrene-butadiene rubber (sSBR) is produced on a very large scale for use in tyre manufacturing. However, the lack of polar functionality in sSBR presents an ongoing challenge and whilst a number of strategies have been used successfully to overcome this challenge, opportunities still exist for the development of facile, scalable approaches to (selectively) incorporate such functionalities into sSBR polymers. The inherent intolerance of living anionic polymerisation towards most functional groups means that functionality is either i) introduced during polymerisation by the use of protected initiators, monomers or terminating agents or ii) after polymerisation via a post-polymerisation functionalization reaction. Terpene monomers such as myrcene and farnesene are bio-available and can be readily (co)polymerized by living anionic polymerisation[1]. Pendant alkenes in the side chain of such polyterpenes offer a valuable opportunity for the introduction of a wide variety of (polar) functional groups. Thus, we present here a (patent pending) post-polymerisation functionalization approach in which statistical terpolymers of styrene, butadiene and myrcene are produced in a one-pot “Fire and Forget” living anionic copolymerisation, whereby the resulting monomer sequence is purely a function of copolymerisation kinetics – an approach we have successfully used for the synthesis of block-like butadiene/styrene/DPE terpolymers[2]. The resulting sSBMR terpolymers are subsequently functionalised via selective epoxidation of the myrcene repeat units. We will describe the copolymerisation kinetics of mixtures of myrcene/styrene, myrcene/butadiene and myrcene/styrene/butadiene, both in a non-polar solvent and in the
presence of TMEDA (a sequence randomizer). Our results show some extraordinarily unexpected (and as yet unexplained) copolymerisation behavior in the presence of the “randomizer”. We will also show that epoxidation of the resulting terpolymer, using mCPMA, is highly selective towards the myrcene repeat units, even in the presence of butadiene.

9:30 a.m.  Highly Stretchable and Responsive Electrode Using Conductive ITO Thin Film Based on Wrinkle Structure - **Hyunsang Lee**, Jeonbuk National University

Traditional metallic and semiconducting electrodes only withstand very limited stretchability. Typically, they are not suitable for stretchable applications. Aimed at this crucial issue, in this study, we used an acrylic rubber sheet (AR) as a substrate and made wrinkle structure using an indium tin oxide (ITO) with 130 nm thickness as a thin film electrode material. The wrinkle structure electrode was fabricated by attaching the ITO film on one phase of the pre-stretched acrylic rubber sheet. While the substrate restored, the ITO film was crumpled and made wrinkle structure due to difference of modulus. Depending on the degree of the pre-strain of the substrate, the wrinkle structure of the ITO film was influenced, and the electrical behavior was also affected. The wrinkle morphology of the AR/ITO electrodes was observed by a scanning electron microscope. The wavelength appeared the uniformed sinusoidal wave which follows the finite-deformation buckling theory. The high degree of pre-strain causes a short degree of the wavelength and the large degree of the amplitude. Also, to prevent from increasing electrical resistance because of the ITO cracks during crumpling, ionic liquids were dropped on the wrinkled ITO surface. The resistance was reduced to almost half after the liquid was dropped. Moreover, the retardation time of the AR/ITO electrodes from 30% strain to 0% is around 10 seconds. To make the time shorter, an acrylonitrile butadiene rubber (NBR) sheet with 300μm thickness was attached at the opposite side of the ITO phase of the AR/ITO electrodes without any deformation. It made the time approximately 2 seconds. To verify the performance of the stretchable electrode, we made a simple Wheatstone bridge sensor in which the voltage was changed by the electrode deformation. The electrodes thus boast wide applications including medical devices and electronics industry.

10:00 a.m.  Break

10:15 a.m.  Enhanced Thermal Conductivity of Thermoplastic Composites with Hybrid Fillers of Polydopamine coated Copper Nanowires and MXene Nanosheets - **Subhadip Mondal**, Jeonbuk National University

Effectively heat conduction pathways are crucial for thermal conductivity of polymer-based composites. In this contribution, we show that thermoplastic polyurethane (TPU) with polydopamine coated copper nanowire (CuNW) / MXene as hybrid fillers could significantly improve the desired properties along with excellent thermal conductivity. Meanwhile, polydopamine coatings help to maintain electrical conductivity of CuNWs whereas CuNWs are usually suffering from deterioration of electrical conductivity. The thermal conductivity of TPU nanocomposites is increased many folds compared to virgin polymer. This is attributed to the formation of the bridging connections and effective heat conduction pathways between CuNWs and MXene nanosheets. Infrared thermal images of the nanocomposites showed good performance to heat dissipation against single filler based composites. In addition, the TPU nanocomposites show excellent mechanical properties and thermal durability. This work may provide a strategy for manufacturing thermally conductive materials for thermal management, particularly when lightweight, flexible, mechanically robust, and electrically insulating thermal conductors are required.
10:45 a.m. Silica Masterbatches Produced with Liquid Phase Mixing Part III. Quasi-static Stress-softening Effect - Liang Zhong, EVE Rubber Institute

The stress-softening effect of rubber-like materials is a phenomenon that the stress required to attain a given elongation is less during the second cycle of deformation. It is generally accepted that both rubber reinforcement by fillers and the failure properties of vulcanizates, such as ultimate strength, tearing, cracking, abrasion, and fatigue, are closely related to the processes of energy dissipation during deformation. In practice, stress-softening effects are used as a quantitative measure of strain energy loss. This paper reports the quasi-static stress-softening effect of the vulcanizates of SBR/BR/Silica masterbatch named EVEC (Eco-Visco-Elastomer composite) produced with continuous liquid phase mixing, taking the silica- and carbon black-filled vulcanizates prepared with conventional technology as references. Compared with the conventional vulcanizates, the EVEC vulcanizate shows rather weak softening effect at low strain and rises rapidly with increasing extension, which could be explained by the effect of the filler agglomeration and polymer-filler interaction. The energy dissipation at low strain is mainly due to the breakdown of filler agglomerates, and at high strain it is attributed to the detachment of the polymer chains from filler surface and rupture of polymer crosslinks and polymer chains in the matrix.

11:15 a.m. Silica Masterbatches Produced with Liquid Phase Mixing: Part IV. Volume Variation and SEM Observation upon stretching - Hao Zhang, EVE Rubber Institute

The volume of vulcanizate varies slightly during stretching. Generally, dilatometer method and hydrostatic weighing method are adopted to measure the volume change. Vacuole formation and the crystallization of polymer molecules are two main origins of the volume variation, which are attributed to the separation of polymer and filler surface and the alignment of polymer molecules, respectively. In this presentation, the relative volume change, \( \Delta V/V \), of EVEC (Eco-Visco-Elastomer composite) produced with continuous liquid phase mixing, is plotted versus elongation, \( \varepsilon \). The volume variation of conventional-mixing counterparts, which are filled with silica or carbon black are also studied. SEM is utilized to directly observe the emergence and variation process of vacuoles during stretching, without replication or ion sputter coating, which will provide images with high fidelity. It is found that the relative volume change of EVEC is much less than that of dry-mixing counterpart, especially after normalized by stress, \( \varepsilon \). SEM images also show that the dispersion of silica in EVEC is better and the amount of vacuoles is much less, characterizing a ""denser"" vulcanizate."

11:45 a.m. Effect of Polymeric Hydrogels in Effluent Treatments - K R Dhanya, CIPET-IPT, Kochi

ABSTRACT IN PROCESS

Characterization of Elastomers - Contributed (Room 2)
Chair: Ed Terrill, Akron Rubber Development Laboratory, Inc.

8:30 a.m. Probing the Viscoelastic Properties of Polymer Composites across Time and Temperature with AFM-based Nano-DMA - Bede Pittinger, Bruker Nano Surfaces

The performance of polymer composites is controlled by the properties of the microstructure of the material as well as its components. As confinement effects and interphase formation can alter properties of the microphases, only measurements performed directly on the composite can provide the needed local property distribution. Mechanical properties of polymers are generally time dependent, so a full understanding requires measurements over a range of frequencies and temperatures. Ideally, one would
like to observe the mechanical behavior of these microscopic domains while they pass through their glass transitions to appreciate the influence of size effects and confinement on time dependent mechanical properties. With its proven ability to map mechanical properties at the nanometer level [1], Atomic Force Microscopy (AFM) has the resolution and mechanical sensitivity needed to investigate these domains. Unfortunately, established AFM measurement modes do not yield results that allow direct comparison to established rheological techniques like Dynamic Mechanical Analysis (DMA). Contact resonance [2] provides mechanical property maps at well-defined frequencies, but cantilever resonances are many orders of magnitude higher than DMA, making comparisons indirect at best. Intermittent contact methods like TappingMode [3], force volume, and PeakForce Tapping [4] face challenges in calculating intrinsic mechanical properties like storage and loss modulus (or tan delta) due to the non-linear process of making and breaking contact [5]. AFM based nano-DMA (AFM-nDMA) provides viscoelastic results that can be directly compared with bulk DMA. Like bulk DMA, it provides spectra of storage and loss modulus across frequency and temperature allowing construction of master curves through Time Temperature Superposition (TTS) [6]. In addition, it allows high resolution measurements localized to the microscopic structures within heterogeneous samples. This presentation will examine the capabilities of this new mode with examples in a wide range of polymers and composites.

9:00 a.m. Online Monitoring of Styrene Butadiene Copolymerization, Including a Final Coupling Reaction – W. Craig Allshouse, Fluence Analytics

A new unique method, ACOMP, of directly monitoring and measuring polymerization processes in real time was tested with SBR. ACOMP yields continuous data on important characteristics of the reaction and resulting polymers. The polymer properties include conversion, molecular weight, reduced viscosity, and shear thinning viscosity. The system yields continuous average values, such as Mw, rather than the intermittent molecular weight distributions (MWD) provided by GPC. The work detailed in this presentation, conducted in conjunction with Bridgestone Research Americas, outlines results obtained from the application of ACOMP to SBR reactions. ACOMP was used to continuously measure the anionic polymerization of styrene butadiene rubber (SBR) at the 20 L scale. The system successfully demonstrated that it can track conversion, along with weight average molecular weight (Mw), and low and high shear reduced viscosities (RV). After the initial reaction, the effects of the coupling agent were directly monitored by ACOMP. This showed a doubling in Mw over time and increases in RV commensurate with what one expects for random coils in a good solvent. ACOMP proved the capability of directly monitoring and characterizing polymer conversion, Mw, and RV of the polymers produced during a living, anionic solution based SBR polymerization process. This information is directly important with respect to characterizing the macromolecular polymer properties of Mw and RV, and it is also useful in providing insights into production rates and efficiencies, such as improving cycle time and yields while achieving product consistency from batch to batch. This information also provides complementary information on the polymers produced which may lead to further correlations to important rheological properties of polymer end products such as Mooney and tan delta. The method can be applied to many other synthetic rubber processes.

9:30 a.m. Insights into the Microscopic Origins of Dynamic Mechanical Properties of Filled Rubber Investigated with X-ray Photon Correlation Spectroscopy - Dillon Presto, The University of Akron

The central role of the structure of the filler network and filler/polymer interactions in determining mechanical properties of nanoparticle-filled rubber is widely appreciated in the
rubber science community. However, despite the importance of this role, much about the connections between microscale filler behavior and macroscale performance remains to be understood. Recent developments in X-ray photon correlation spectroscopy (XPCS) allow us to probe the microscale dynamics of filler particle networks and determine how this influences macroscale properties. We have used in-situ XPCS on styrene-butadiene rubber (SBR) filled with silicas of different surface chemistries under dynamic strain to probe the rearrangement of the filler network. We draw connections between the filler/polymer interaction and the resulting network structure, filler dynamics, and macroscopic properties.

10:00 a.m. Break

10:15 a.m. Characterisation of Friction Behaviour for Dynamic O-ring Seals During Cyclic Testing Under Extreme Pressure and Temperature Conditions - Eduardo Yanes, Queen Mary University of London

Elastomer friction behavior has been studied for decades, mostly for applications in the tire industry. Working conditions for car tires are low pressure and high roughness due to asphalt and even off-road tracks. The oil industry uses these models of frictional behavior but they are not in any way correspondent with the actual conditions of elastomeric seals that are put on service. Temperatures of up to 150°C and 70 MPa are not uncommon in downhole environments. The effect of hydrostatic pressure will act not only on the mechanical behavior of the material but will be transferred as contact pressure against the sealing surface. O-ring type elastomer seals are common in many different industries. Friction plays a critical role during the setting and in service of these components. An experimental O-ring friction testing rig has been developed that can measure the effects of speed and hydrostatic pressure on elastomer friction using various types of fluid environments. In this paper the friction rig uses industry standard dimensions for the O-ring size, the interfacing gland, the compression levels, extrusion gap size and pressure rating. The measured friction force is divided by the normal force as determined using an FEA approach. This is then used to calculate the experimentally measured coefficient of friction. Results are then plotted as friction against pressure and friction against speed. The discussion is focused on the effect of surface roughness, lubricant viscosity and hydrostatic pressure.

10:45 a.m. Investigation of Polymer-Silane Coupling in Model Natural Rubber-Silica/Silane Systems - Claude Arreyngang Tabe, Deutsches Institut für Kautschuktechnologie e. V. (DIK)

The use of SBR-silica-silane systems for passenger car tires is state of the art and has high advantages in the performance, especially with regards to rolling resistance and wet traction. However, NR-silica-silane systems are up to now not yet efficient. So liquid chromatography mass spectrometry (LC MS), size exclusion chromatography (SEC), and direct injection mass spectrometry (DIMS) were employed to study the coupling reaction between natural rubber and silanes using squalene as a model compound for natural rubber. Squalene/silane coupling products were formed from the reaction of squalene with bis(triethoxysilylpropyl)tetrasulfide (TESPT) and bis(triethoxysilylpropyl)disulfide (TESPD) silanes, with the TESPT silane donating active sulfur to form thiols and a dimer with squalene. TESPD silane could only form squalene/silane products through thermal cleavage of its di sulfidic bond. These reaction products could also be qualitatively identified in analysis using SEC. As for the triethoxy octyl silane (OCTEO), no reaction products were formed in its reaction with squalene. A better understanding of the coupling reaction between silanes and natural rubber will bring more insight into the compounding and vulcanization processes in silica/silane systems. This might go a long way to control
processes such as pre scorch and also to enhance the reinforcement of silica/silane systems in natural rubber.

11:15 a.m. Rheology and Flow Instabilities of Polypropylene/Ethylene Propylene-Diene-Monomer (PP/EPDM) based Thermoplastic Vulcanizates - Savvas Hatzikiriakos, The University of British Columbia

Thermoplastic vulcanizates (TPVs) are a special class of polymer blends of polypropylene (PP) and EPDM rubber in which a high content of rubber (EPDM) is simultaneously crosslinked and dispersed in a thermoplastic matrix (PP). Due to the presence of rubber, their rheology is complicated presenting characteristics similar to those of soft solids. Moreover, they exhibit flow instabilities in extrusion such as sharkskin and gross melt fracture depending on the molecular characteristics and architecture of their constituents and composition. In this study, the rheology of several TPVs is studied in terms of the rheology of their primary constituent components (PP and EPDM) by using an integral constitutive equation (K-BKZ). Their processing as can be assessed by capillary rheometry is examined as a function of temperature and shear rate in terms of critical shear rates and stresses for the onset of melt fracture phenomena. Correlations between these critical values and the molecular characteristics of TPVs are also developed and discussed.

11:45 a.m. Mechanical and Structural Investigation of Thermoplastic Vulcanizes Using Molecular Dynamics Simulations - A O Wang, Northwestern University

We studied the tensile deformations of ethylene propylene diene monomer rubber (EPDM) and semicrystalline polypropylene (PP) using atomistic molecular dynamics simulations to understand the effect of composition, crosslink density, and microstructure on mechanical behavior at varying strain rates. Sweeping through different EPDM composition ratios, a positive correlation was observed between ratio of propylene monomer and modulus of EPDM at high strain rates. Calculation of the Debye-Waller factor indicated that the higher propylene ratio hinders the local segmental motion of monomers, contributing to higher moduli at high strain rates. Factors that reduce the Debye-Waller factor, such as crosslinking or increased PP content generally result in higher moduli. Additionally, the rate-dependence of mechanical properties for both EPDM and PP was quantified. We also observed higher entanglements number per chain with higher ethylene monomer ratio, resulting from the lower entanglement molecular weight of polyethylene than that of polypropylene. Investigations on semicrystalline polypropylene domains revealed that when lamellae are stretched along the chain direction, localized slip out of chains can be observed, whereas bulk shear deformation prevails at lower rates. Both situations cause stress softening under high strain. Stretching the polypropylene lamellae along the lamellae growth direction (up to 500% strain), we observed chain buckling within the crystalline phase, followed by realignment of the chains towards the stretching direction. This mechanism causes strain hardening under large deformations. Our findings illustrate some of the important molecular mechanisms underpinning the constitutive behavior of thermoplastic elastomers and pave the way for multi-scale analyses linking composition and microstructure to performance.