NIST/Industry Polymer Surface/Interface Consortium Workshop
April 17, 2017 (Monday)
NIST, Gaithersburg, MD
Conference Room: B205-9/226

Industrial Practice and Scientific Exchange (Invited presentations)

8:30- 9:45a	Social networking
8:45- 9:00a	**Welcome** Division Chief – Jason Averill ***Materials and Structural Systems Division***, **EL/NIST**
9:00- 9:40a	**Accelerated Weathering Parameters for Aromatic Polymers** Dr. Jim Pickett, ***SABIC***
9:40 – 10:10a	**How Long Should I Run My Weathering Test to Reproduce 1 Year of Outdoor Aging?** Dr. Olivier Rosseler, ***Saint-Gobain***
10:10 – 10:40a	**Automotive Perspective: How Long Should I Run My Weathering Test to Reproduce 1 Year of Outdoor Aging?** Dr. Michael Koerner, ***Axalta Coating Systems***
10:40 – 11:00a	Break
11:00– 11:40a	**Challenges in Accelerated Weather Testing, Method Development and Service Life Prediction of Exterior Commercial Airplane Coatings** (via Webinar) Dr. Kady Gregersen, ***Boeing Research & Technology***
11:40– 12:10a	**Continuous Measurement of Protective Properties of Coatings in Dynamic Environments** Dr. Fritz Friedersdorf, ***Luna Innovations Incorporated***
12:20- 1:20p	Lunch at NIST Cafeteria
1:30 – 2:30p	**Tour: Net-Zero Energy Residential Test Facility** Dr. David Yashar, Deputy Chief ***Energy and Environment Division, EL/NIST***
2:30– 2:50p	Break
2:50- 3:20p	**Coating Appearance Fundamentals – Relating Surface Microstructure to Wave Scan Data** Dr. Robert Farina, ***Eastman Chemical Co.***
3:20 – 3:50p	**Aging of CNT-reinforced Hierarchical Composites** Dr. Ajay Krishnamurthy, ***MML/NIST***
3:50- 4:20p	**The Performance and Durability of Graphene Oxide/Polymer Nanocomposites** Dr. David Goodwin, ***EL/NIST***
4:20 -4:40p	**Tour: SPHERE (short tour)- longer one – on Tuesday afternoon**
5:30 p	Dinner at local Restaurant (Firebirds Wood Fired Grill) https://gaithersburg.firebirdsrestaurants.com/menus/

Accelerated weathering parameters for aromatic polymers

Olga Kuvshinnikova,[1] James Pickett,[1] and Li-Piin Sung[2]
[1]SABIC, [2]Engineering Lab/NIST

Abstract: Plastics and coatings used outdoors degrade from the effects of sunlight, heat, moisture, and other factors. Service life prediction requires detailed knowledge of how these materials respond to the irradiance, temperatures, and moisture conditions of accelerated laboratory exposures so that test results can be extrapolated to real-world exposures. The NIST SPHERE is an ideal instrument for quantifying these effects because it can control several levels of conditions in multiple sample positions with accuracy and precision. Four commercially important engineering thermoplastic resins, polycarbonate (PC), poly(butylene terephthalate) (PBT), a PC/PBT blend, and poly(styrene-co-acrylonitrile) (SAN) are currently being tested in the SPHERE at several combinations of irradiance, temperature, humidity, and UV wavelength. Preliminary results reported here both confirm some previous findings and provide some new, surprising information. The learnings will be applicable to the development of new test methods and, eventually, new industry standards.

Bio: James E. Pickett received his BA in Chemistry from Kalamazoo College in 1976 and a Ph.D. in Organic Chemistry from Yale University in 1980 where he worked with Professor Harry H. Wasserman on the organic chemistry of singlet oxygen. He joined GE Corporate Research and Development in 1980 where he worked as a staff chemist, unit manager, senior scientist and principal scientist until his retirement in June, 2014. He was named a GE Coolidge Fellow in 1999. Since his retirement he has worked as a consultant for industry. Much of his research at GE was focused on the degradation and stabilization of polymers such as poly(phenylene oxide) and polycarbonate, design of highly weatherable coatings and polymers, accelerated testing, and lifetime prediction. He is the author or co-author of about 60 publications and has been awarded 61 U.S. patents.

How long should I run my weathering test to reproduce 1 year of outdoor aging?

Dr. Olivier Rosseler, ***Saint-Gobain***

Abstract: Isn’t it funny how sometimes the simplest questions can have the most complex answers? The most frequently asked questions when it comes to aging tests probably is “How long should I run this accelerated test to reproduce 1 year of aging?”. A simple question that our community has been investigating for dozens of years. A simple question that only has one good answer: “Well… it depends”.

However, that answer is not good enough and we need to come up with something better. For that purpose, we have developed a UV calculator that estimates the amount of UV radiation a product is exposed to over the course of 1 year, as a function of location, tilt angle and orientation. We can then calculate an equivalent lab test duration to reproduce the same UV dose in standard weathering tests. However imperfect, this solution provides an estimate of a worst case scenario to guide lab weathering test practices.

Bio: Olivier is a principle scientist in the central R&D division of Saint-Gobain, working on test method development, failure mode analysis and lifetime estimation. He received his Ph.D. in materials science from the University of Strasbourg in France and completed a 2-year post-doc at the Lawrence Berkeley National Lab where he helped develop the rapid rating method, which predicts the loss of solar reflectance of roofing products in natural aging.

Automotive Perspective: How long should I run my weathering test to reproduce 1 year of outdoor aging?

Dr. Michael Koerner, ***Axalta Coating Systems;*** michael.r.koerner@axaltacs.com, 302.407.4398

Abstract: Typical automotive coatings include electrocoat, primer, basecoat and clearcoat where each layer has a role to protect the over film integrity. Most OEM vehicle manufactures use outdoor Florida weathering as the "gold standard" to certify durability of coating systems they should approve. As coating formulators with more urgent business and technical needs, we are often asked, "How long should I run my weathering test to reproduce one year of outdoor aging?"
Unfortunately the answer is, "it depends." In this talk, we cover several coating system failure modes and the challenges we face in trying to predict outdoor weathering results.

Bio: Mike Koerner is a Technical Fellow currently leading the waterborne colorcoat development team as part of Axalta Research & Development in Wilmington, DE. After earning Chemical Engineering degrees from Drexel and Princeton, he started work at DuPont in 1987. Most of his career has been spent developing products and supporting Automotive OEM coatings business in North America, Europe and Asia. Throughout his professional career Mike has ongoing interest in all things rheology, especially on effects at a colloidal scale.

Challenges in Accelerated Weather Testing, Method Development and Service Life Prediction of Exterior Commercial Airplane Coatings

Kady Gregersen**,** Boeing Research & Technology

Abstract: Exterior commercial airplane coatings systems serve decorative and protective functions. Coatings must retain gloss and color in-severe service environments. Commercial aircraft can make up to eight flights per day and cruise at altitudes as high as 13 km for up to 16 hours per day. Ultraviolet (UV) radiation exposure can increase by a factor of 4, paint surface temperatures can range from 75ºC to -60ºC between ground and cruise altitudes, and moisture levels vary greatly as well. Any accelerated test method or model for service life prediction of coating systems must take into account the effects of the changes in UV radiation, temperature, and moisture on photo-oxidation and hydrolysis. Comparison of sensitivity of damage from overlap of polymeric absorption peaks with UV spectral radiance measured at cruise altitudes of 9.1 to 12.2 km, at ground level in southern Florida, and produced by xenon arc lamps with various filters (as specified in SAE J2527 and ASTM D7869) is presented. Gloss and color shift data are then assessed for coatings using exposures in southern Florida, SAE J2527, and ASTM D7869.

Bio: Kady Gregersen received her BS in chemistry from the College of William and Mary. She then pursued a masters at Ohio University in physical chemistry studying the thermodynamics of ice nucleation. Finally, she obtained her PhD from the University of Washington in materials chemistry doing materials development for biological applications. She began her career at Boeing in a computational modeling group working on materials development for composites. The last 3 years she has been working in the paints and coatings group on coating durability and new product development.

Continuous Measurement of Protective Properties of Coatings in Dynamic Environments

Fritz Friedersdorf, Luna Innovations Incorporated

Abstract: Organic coatings with corrosion inhibitors are the primary means of protecting structures from atmospheric corrosion in harsh environments. Environmental compliance and a desire for increased performance and functionality continue to drive coating development and new product introductions. Luna is engaged in a number of programs related to understanding atmospheric corrosion, developing accelerated tests, and modeling degradation processes. Novel continuous measurements of corrosion rate and coating barrier properties are used to relate instantaneous environmental parameters to coating condition and degradation kinetics. These measurement methods have been standardized and are compliant with the ANSI/NACE TM0416-2016 for monitoring atmospheric corrosion and coating performance. A review will be given of the sensing methods and systems being used to measure free corrosion, galvanic corrosion, and coating properties in laboratory and outdoor environments. Measurements in cyclic testing and outdoor exposures have demonstrated that hysteresis effects are important in wetting and drying of surfaces and that these dynamic conditions control moisture content in the coatings and accelerate corrosion of coated materials.

Bio: Fritz Friedersdorf received his Ph.D. in Materials Science and Engineering from The Johns Hopkins University. Fritz joined Luna Innovations in 2002 and is the Director of the Intelligent Systems Group where he has been responsible for over 50 funded projects on materials development, structural health monitoring, and corrosion testing and measurement. Fritz has numerous publications and 14 patents and patent applications. He is a member of NACE International and is the US Chair to ISO Technical Committee 156 - Corrosion of Metals.

Coating Appearance Fundamentals – Relating Surface Microstructure to Wave Scan Data

Robert Farina, Ph.D., P.E. – Eastman Chemical Company

Abstract: In this work, we have developed an approach to compare the surface microstructure of a coating to wave scan data obtained using a BYK Wave-Scan Dual instrument. Several appearance analysis case studies using bell sprayed panels will be presented to demonstrate the consistency and uniqueness of our approach. The primary objectives of this work were to compare wave scan data with enhanced imaging and analytical software analysis, as well as to

highlight appearance differences between coatings containing Eastman resin compared to coatings with alternative commercial resins. Coating surfaces were imaged using a Basler Line Scan Camera at length scales large enough to observe microstructure features in the Long Wave (LW) and the Short Wave (SW) spectra of wave scan data. Features, or undulations, on the surface of the coating were then analyzed with LabVIEW software, and were isolated into features of various sizes consistent with LW and SW data using Fast Fourier Transform (FFT) bandpass filters. Optical profilometry using a Bruker ContourGT was also performed to obtain height, or surface roughness, information to support optical measurements. These images were processed using Bruker's Vision64 software, also using FFT bandpass filters, to isolate features consistent with wave scan data ranges. In select case studies, rheology data was collected to understand the flow and leveling behavior of the formulations in correlation with appearance analysis. The results of our work show direct correlation between wave scan data and feature analysis using our imaging and image processing techniques.

Bio: Rob Farina obtained his Ph.D. in Chemical Engineering from the University of California – Santa Barbara in 2012, where he studied polymer physics with Professor Matt Tirrell. He then served as a Senior Associate at Exponent Failure Analysis Associates working in the field of Polymer Science consulting, and now serves as a Senior Application Coatings Scientist at Eastman Chemical Company.

Aging of CNT-reinforced hierarchical composites

Ajay Krishnamurthy, MML/NIST

Abstract: As CNT based composites are increasingly explored as viable candidates for structural applications, it is important to understand and characterize their properties as a function of various aging conditions. In the current study, a hybrid "fuzzy" fiber composite was manufactured and its performance was evaluated against plain fiber composites after exposure to deionized water at two different temperatures (60 ^{o}C, and 25 ^{o}C) for different exposure times (15 days, 90 days and 6 months). The CNT nanofibers were incorporated into fiber composites by directly adhering MWCNTs (using chemical vapor deposition) to a model, Al_2O_3 textile fiber and infiltrating the fiber stack using a high glass transition temperature (T_g), epoxy resin (RTM6).

Our findings indicate that at high temperatures (60 ^{o}C), plain fiber composites rapidly lose their mechanical strength by up to 45 % in a time span of 15 days, while CNT composites retain their strength and electrical properties during the entire experimentation period (90 days). At room temperature conditions (25 ^{o}C), both composite types do not exhibit loss of properties up to a 6-month duration. The locus of failure was explored by three hypotheses, namely polymer degradation, fiber degradation, and interface failure. Using various characterization techniques such as Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR), differential scanning calorimetry (DSC), x-ray diffraction (XRD), and scanning electron microscopy (SEM), polymer degradation and fiber degradation were eliminated as primary causes of failure. Thus, it was concluded that the plain fiber composites predominantly failed by interface debonding caused by the presence of interfacial water at high temperatures. However, the secondary CNT nanofiber reinforcements within the fuzzy fiber composites strengthen the CNT/polymer interface via CNT pullouts, CNT fractures, and crack bridging, which allowed the fuzzy fiber composites to withstand these harsh environments for extended periods of time.

Bio: Ajay Krishnamurthy received his PhD in Mechanical Engineering in 2014 from Rensselaer Polytechnic Institute under the guidance of Prof. Nikhil Koratkar. His dissertation was focused on the use of few-layer graphene coating for an anti-corrosion application. During this period, Dr. Krishnamurthy has accrued extensive experience in synthesis, characterization and application of single and few-layer graphene in corrosion coatings, battery electrodes and structural composites. His paper on "Passivation of microbial corrosion using a graphene coating" was picked as part of Editor's choice in Elsevier® Carbon.

Since 2015, Dr. Krishnamurthy has been a guest researcher at National Institute of Standards and Technology, working under the guidance of Dr. Aaron Forster. At NIST, Dr. Krishnamurthy has worked extensively on evaluating the properties of CNT based hierarchical composites as function of aging environments. Dr. Krishnamurthy is currently involved in characterizing polymer structural porosity using positron annihilation lifetime spectroscopy, evaluating rheological properties of CNT based composites, and sensing small strain damage in CNT reinforced composites.

Select Publications:

1. Krishnamurthy A, Gadhamshetty V, Mukherjee R, Chen Z, Ren W, Cheng H-M, et al. Passivation of microbial corrosion using a graphene coating. Carbon N Y 2013;56:45–9. doi:10.1016/j.carbon.2012.12.060.
2. Krishnamurthy A, Gadhamshetty V, Mukherjee R, Natarajan B, Eksik O, Ali Shojaee S, et al. Superiority of Graphene over Polymer Coatings for Prevention of Microbially Induced Corrosion. Sci Rep 2015;5:13858. doi:10.1038/srep13858.
3. Mukherjee R, Thomas AV, Krishnamurthy A, Koratkar N. Photothermally reduced graphene as high-power anodes for lithium-ion batteries. ACS Nano 2012:7867–78.
4. Eksik O, Maiorana A, Spinella S, Krishnamurthy A, Weiss S, Gross RA, et al. Nanocomposites of a Cashew Nut Shell Derived Epoxy Resin and Graphene Platelets: From Flexible to Tough. ACS Sustain Chem Eng 2016:acssuschemeng.5b01684. doi:10.1021/acssuschemeng.5b01684.
5. Natarajan B, Orloff ND, Ashkar R, Doshi S, Twedt K, Krishnamurthy A, et al. Multiscale metrologies for process optimization of carbon nanotube polymer composites. Carbon N Y 2016;108:381–93.
6. Salehi M, Krishnamurthy A, Forster AM, Hsiao K--T, Whelton AJ. Polyester composite water uptake and organic contaminant release affected by carbon nanofiber reinforcements. J Appl Polym Sci 2016;133.

The Performance and Durability of Graphene Oxide/Polymer Nanocomposites

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**Biosystems and Biomaterials Division, Materials Measurement Laboratory

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Abstract: GO is a good nanofiller candidate for water-borne polyurethane (WBPU) coatings since GO has outstanding physicochemical and mechanical properties, disperses in water, and is relatively low in cost. However, the durability of GO/polymer nanocomposites (PNCs) is unknown and can potentially impact the service life and environmental health and safety of

WBPU coatings, especially if GO release occurs. Therefore, this research measures the performance properties and degradation behavior of GO/WBPU nanocomposites to assess the benefits and limitations of GO nanofillers, with a focus on their use in coatings to prevent corrosion. Specifically, GO/WBPU nanocomposites were prepared at different GO loadings and characterized with laser scanning confocal microscopy (LSCM), scanning electron microscopy (SEM), and Raman spectroscopy. To assess material performance, the mechanical strength, thermal properties, and corrosion resistance of GO/WBPU nanocomposites were measured. Relative to unfilled WBPU, GO/WBPU nanocomposites were shown to have superior performance properties, with the exception of water uptake at high humidity. Accelerated weathering of GO/WBPU nanocomposites was achieved by GO/WBPU exposure to a highly collimated, uniform flux of ultraviolet (UV) light under controlled temperature and humidity conditions (NIST SPHERE). Released materials were collected from the surface using simulated rain and analyzed with UV-Visible spectroscopy, Raman spectroscopy, and microscopy. Minimal GO release was observed under both dry and wet conditions. Overall, the enhanced durability and performance properties observed for GO/WBPU nanocomposites relative to unfilled WBPU suggest that GO is a viable nanofiller for WBPU coatings.

Bio: **David G. Goodwin Jr., Ph.D.**

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David G. Goodwin Jr., Ph.D. is a research chemist in the Polymeric Materials Group at the National Institute of Standards and Technology. He is a National Research Council (NRC) postdoctoral associate working on polymer composite durability and performance. David's NRC project involves the exposure of polymer nanocomposites containing graphene oxide to accelerated weathering conditions to evaluate the changes in the surface chemistry of the material as well as to develop metrologies for nanomaterials that are released during this process. His research is moving towards the durability of carbon fiber/polymer composites for use in infrastructure applications. David's training lies in surface analytical chemistry, nanomaterial and nanocomposite characterization, and environmental chemistry. At Johns Hopkins University, David defended his Ph.D. dissertation on the "Interactions of Microorganisms with Carbon Nanotube/Polymer Nanocomposites" in the Department of Chemistry. The interdisciplinary research carried out during his Ph.D. involved many aspects of materials science engineering, environmental engineering, and microbiology. David graduated with a B.S. in Chemistry from Lafayette College in Easton, PA where he conducted research on the mechanism behind the Scott test for cocaine, a preliminary test used in the field by police.